THE
PROCEEDINGS
OF
THE PHYSICAL SOCIETY

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THE PHYSICAL SOCIETY

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THE PHYSICAL SOCIETY

1 LOWTHER GARDENS, EXHIBITION ROAD, LONDON, S.W. 7.

THE 200-INCH TELESCOPE

By H. SPENCER JONES, M.A., Sc.D., F.R.S.

Astronomer Royal

Twelfth Thomas Young Oration, delivered 30 *May* 1941

§1. INTRODUCTION

No instrument intended solely for scientific research has aroused greater interest amongst the general public than the 200-inch telescope. The progress of its construction has been closely followed, not merely in the United States but throughout the world. Though an attempt to do something that has not been done before, or to achieve something on a much larger scale than previously, is always likely to arouse interest, it is not mainly, I think, for this reason that the construction of the 200-inch telescope has captured the popular imagination. It is due rather to a realization of the immensity of the Universe and to the expectation that, by probing farther into its remote depths, an answer may be found to some of the still unsolved problems of the Universe.

The largest telescope previously built, the 100-inch reflector of the Mount Wilson Observatory, was completed in the darkest days of the last war. On the night in the year 1917, when the first trials of the completed instrument were being made, came the news of the disastrous Italian defeat at Caporetto. In the years that have since elapsed, our views of the Universe have been revolutionized. It is sufficient merely to recall that, at that time, it was still undecided whether the so-called spiral nebulae were constituent parts of our Milky Way or galactic system or whether they were island universes, remote in space, generally comparable to our own galactic system. Many astronomers were of the one opinion; many were of the other. The 100-inch telescope provided the answer to this and to many other problems. But for every question that it answered there were many others suggested, which it could not answer. The 100-inch telescope has photographed universes so distant that, even with its aid, the eye of man cannot see them; they are revealed as faint smudges on photographs with long exposures on sensitive plates. Light, ever more light, is the need before more can be learnt about these distant systems, and still larger telescopes the way to supply the need.

The importance of larger telescopes to make possible advances in astronomy in certain directions was fully realized by Dr. George Hale, Director of the Mount Wilson Observatory. When, in 1927, after ill-health had caused him to resign the directorship, the Editor of *Harper's Magazine* invited Hale to contribute an astronomical article, he chose as his subject " The Possibilities of Large Telescopes ". In the course of this article he wrote :

" Like buried treasures, the outposts of the Universe have beckoned to the adventurous from immemorial times. Princes and potentates, political or industrial, equally with men of science, have felt the lure of the uncharted seas of space. If the cost of gathering celestial treasure exceeds that of searching for the buried chests of a Morgan or a Flint, the expectation of rich return is surely greater and the route no less attractive .... I believe that a 200-inch or even a 300-inch telescope could now be built and used to the greater advantage of astronomy .... Lick, Yerkes, Hooker and Carnegie have passed on, but the opportunity remains for some other donor to advance knowledge and to satisfy his own curiosity regarding the nature of the Universe and the problem of its unexplored depths."

A proof of this paper was sent to Dr. Wickliffe Rose, President of the Rockefeller General Education Board, and led within a few weeks to a gift of six million dollars to the California Institute of Technology for a 200-inch telescope, together with a complete astrophysical observatory, with laboratories, workshops and auxiliary equipment. Rarely can a magazine article have been so productive of result.

To have obtained the financial provision for the construction of a 200-inch telescope removed the first and the least of the difficulties. The many problems involved in proceeding in one step from a 100-inch telescope to one of double the aperture had then to be solved; the doubling of the aperture enormously increased the difficulties.

§ 2. DESIGN OF THE MIRROR

The fundamental and the most difficult of the problems was the construction of a mirror of 200-inch diameter. The mirrors of the early reflecting telescopes were made of speculum metal, a hard and brittle alloy of copper and tin containing about one part by weight of tin to two of copper. Speculum metal will take a high degree of polish and has a moderately good reflecting power. It is difficult to cast and anneal, unless the copper content is increased, in which case the mirror is liable to develop a tarnish which can only be removed by repolishing and re-figuring. The largest speculum mirror ever made was the 6-foot mirror of Lord Rosse's great reflector, completed in 1851. The discovery by Liebig of a simple chemical process by which a thin film of silver could be deposited on a glass surface made possible the silver-on-glass mirror. The application of Liebig's discovery to glass mirrors and the methods of making and testing such mirrors were due primarily to Foucault in the 'sixties of last century, and since that time glass mirrors have entirely superseded speculum mirrors.

Glass has two important advantages as a material for mirrors: it can take a very high degree of polish and it is free from any liability to warp or distort with age. But it suffers from two great disadvantages, which make it far from an ideal material; it has a high coefficient of expansion and it is a poor conductor of heat. When a glass mirror is in use, changes and inequalities of temperature give rise to localized expansions and contractions which impair the figure of the mirror, change the focus and deform the images. Because the heat conductivity is low, temperature differences within the mirror persist for a long time.

For the same reasons, large glass mirrors are difficult to cast and to anneal. In order to obtain sufficient rigidity, it is customary for the thickness of the mirror to be about one-eighth of its diameter. The 100-inch mirror weighs about five tons. After casting, the mirror must be annealed, to relieve internal strains, by cooling at a rate so slow that at any stage the temperature throughout the mass must be practically uniform. A disk of 100-inch diameter requires several months' annealing, and even then there is a considerable risk that, when the annealing oven is opened, the disk will be found to be in fragments. There were, in fact, several failures to produce a satisfactory 100-inch disk, and, in the end, the one disk which had been successfully annealed, but which had been initially discarded because it contained many bubbles and imperfections, had to be used.

The 100-inch disk was made at the St. Gobain glassworks of ordinary plate glass. A 200-inch disk of similar glass, with the same ratio of thickness to diameter, would weigh 40 tons, and it was estimated that to avoid the risk of fracture during annealing, the annealing would need to be extended over nine years. It therefore became necessary to examine every possible alternative. One alternative was a built-up mirror instead of a solid disk, enabling a great saving in weight to be made without sacrifice of rigidity, and thereby simplifying considerably the problem of the annealing. The idea was not a new one. It had been tried nearly a century previously by Lord Rosse, who constructed a three-foot speculum mirror of cellular form, the reflecting surface being supported by a metal ring with radial and transverse stiffeners, dividing the back of the mirror into compartments, in which the air could circulate freely. The mirror was not a success: the images were not satisfactory, the supports at the back revealing themselves by defects in the optical surface. The idea was revived by Ritchey in 1924, who constructed a 60-inch disk of small plates of glass cemented, in the form of a honeycomb structure, to a top plate; the polished surface, however, showed the same defects. Pressure in polishing caused a flexure of the glass at the centre of each cell. For this reason, and because there were doubts whether such a mirror would keep its figure, this idea was not further entertained.

The possibilities of metal mirrors were considered, and many special alloys were suggested. A metal mirror, with a thin layer of glass of the same coefficient of expansion fused to its surface, was proposed by the Philips Lamp Works, of Eindhoven, Holland, and a small mirror of this type was tried. A mirror made

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of stainless steel was seriously considered, and several samples of stainless steel were examined. Stainless steel has the advantage of high heat conductivity, freedom from tarnishing and high reflectivity in the ultra-violet. The great drawback to a large mirror made of metal would be its weight; it is doubtful, moreover, whether permanence of figure could be guaranteed. Much experience would be necessary with smaller mirrors of so experimental a nature before it would be known whether they would meet the rigid requirements. It is possible that a light alloy might be found that would prove suitable for astronomical mirrors, and there is much scope for experiment in this direction ; but it seemed unwise to hazard a 200-inch mirror in so untried a field and in default of long experience with mirrors of smaller size.

Two possibilities that were less in the nature of untried innovations were open. These were to make the mirror either of fused silica, which has a very low coefficient of expansion, or of the glass of high silica content, known as Pyrex, which has a coefficient of expansion about one-third that of plate glass. The prospect of a large mirror of fused silica was an inviting one; its insensitiveness to temperature changes would eliminate many troubles. Disks of small size had been successfully made of fused silica, and the General Electric Company was confident that a large mirror could be made. The services of the Company's research laboratory were offered on the basis of the cost of time and materials, without any additions for overhead charges. The contract for the work was placed on this basis.

The process consisted in melting the purest quartz sand obtainable, without any flux, in a circular electric furnace, which formed the mould. A temperature of 3000° F. is needed to fuse the quartz. Fused quartz is very viscous and passes into vapour before it becomes thoroughly liquid, so that it is impossible to get rid of the large number of minute air bubbles that are trapped in it, even when vacuum pumps are continually pumping out the air above the quartz. The quartz disks thus obtained have a pearl-grey appearance, because of the air bubbles, and it is impossible to obtain a satisfactory optical surface from them. The disk to be made in this way was to be ground to the approximate curvature required; the second part of the process was to coat it to a sufficient thickness with a layer of transparent fused quartz, entirely free from air bubbles. The first method of producing the transparent layer was to cover the disk with slabs of clear quartz, a few inches square, and to weld them together with a blow-torch. The small slabs were made by welding pure quartz crystals in a special furnace; with great care it was possible to get them to run together into a single mass free from bubbles. It was found to be impossible to produce larger slabs free from the troublesome bubbles. Though by this method disks of small size, with a surface layer of clear quartz, were successfully made, the method failed when larger disks were attempted. The larger the surface, the more difficult it proved to weld the slabs evenly together, and it was evident that some different method would have to be devised for making a 200-inch disk.

Attempts were therefore made to produce the clear coating by spraying pure crystalline quartz, ground into a fine dust, on to the surface by means of an oxy-hydrogen flame. The rain of quartz droplets froze on the surface in a clear layer and disks up to two feet in diameter were successfully made. But the difficulties increased rapidly with the size of the disk. Much experimenting was carried out to ensure success; multiple nozzles, circling slowly round inside the furnace, were tried to ensure a uniform coating. There was no inherent reason why a 200-inch quartz disk should not ultimately have been successfully produced, but at a price. It was the price that put an end to the experiments; the cost would have been at least one million dollars, and probably much more. It seemed possible that the whole of the grant might be used up in making the mirror. The use of quartz was therefore reluctantly abandoned in favour of Pyrex glass.

The ordinary Pyrex glass, of which cooking utensils are made, has a coefficient of expansion about four times that of quartz but only one-third that of plate glass. Its use for domestic purposes shows that it can withstand large and rapid changes of temperature. With a larger percentage of silica, glass with a lower coefficient of expansion is possible, though the glass becomes more viscous, harder to melt and harder to cast as the silica content is increased. At the research laboratory of the Corning Glass Works, experiments were made to find to what extent the proportion of silica in the glass could be increased, without making the glass too difficult to use. The special low-expansion Pyrex glass, finally decided upon, had a coefficient of expansion one-quarter that of plate glass, three times that of quartz. The high silica content of this glass greatly reduces the time required for satisfactory annealing and thereby reduces the danger of devitrification, which is liable to occur when the annealing process is long.

A glass disk 200 inches in diameter and 30 inches in thickness would weigh about 40 tons. The problems involved in building a telescope sufficiently strong and rigid to carry such a weight and to be free from serious flexure effects were considerable. It was suggested by Dr. Day, of the Geophysical Institute, Washington, that the disk should be designed with a thin face supported on a ribbed back, the ribs being arranged to provide adequate stiffness. Not only would the weight be reduced and the mechanical problems of the design of the telescope be simplified, but the effects of changes of temperature would be reduced. The ribbed structure at the back of the disk would also simplify the design of the supports for the mirror. The mounting of the 100-inch mirror had recently been redesigned. The mirror rested in the telescope on a number of cast-iron pads, supported by counterpoised levers. These introduced friction when the mirror was turned from one position to another, causing strains and deterioration in the quality of the star-images. When the mirror was remounted with pads fitted to its back, which were supported by ball bearings on the counterpoised pads, the friction was eliminated and the quality of the images improved. The cells at the back of a ribbed mirror would be ideal for containing similar ball-bearing supports.

The ribbing, which is clearly seen in figure 1, was designed by Mr. Pease of the Mount Wilson Observatory. The main part of the disk was to be 5 inches thick; on the back of this there would be 36 cylindrical pockets, forming the corners of a network of equilateral triangles, whose sides formed the ribs. A ribbed coelostat mirror, made at the Corning Glass Works, was subjected to very severe tests in the Optical Shop in Pasadena and proved entirely satisfactory.

Meanwhile, investigations were being undertaken at the Research Laboratory of the Corning Glass Company to devise methods for casting and annealing large disks, and to find suitable materials for building the mould and cores and the best means of anchoring the cores. The high melting temperature of the
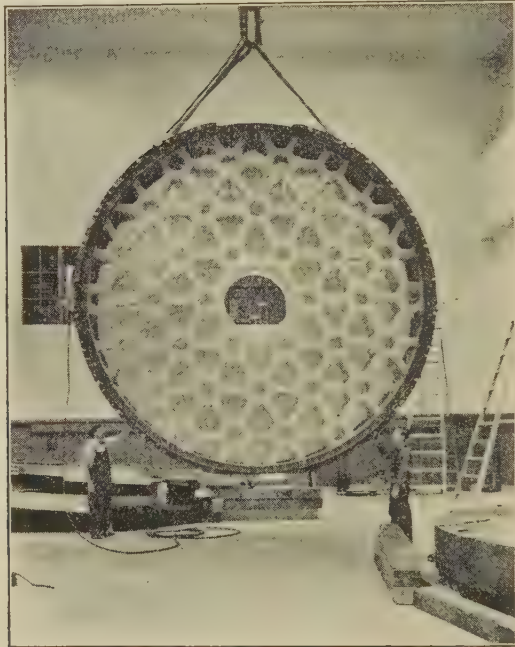
Figure 1.   The completed 200-inch disk, after arrival at Pasadena.

special Pyrex glass caused difficulties that were absent at the lower melting temperature of plate glass. Fire bricks of high quality, from which satisfactory moulds for casting plate glass were made, proved useless because they absorbed moisture which turned to steam when the glass was poured in, filling the glass near the walls with bubbles. In the end, bricks of pure white silica were used. They were made from blocks of ground-up cork, sand and water mixed together; these blocks were fired in a kiln, when the cork burned out, leaving hard, porous bricks, which absorbed no moisture, were resistant to the high temperature of the molten Pyrex and enabled the glass to " breathe " by allowing any air or gas in it to escape through the pores.

The usual method of casting large mirrors had been to pour the molten glass into an open mould, the furnace being tapped and the glass running from it along a trough into the mould. The special Pyrex glass could not be poured in this way; it rapidly chilled sufficiently to stop the flow. It was therefore decided to fill the mould by ladling the glass into it from the furnace. Experiments soon showed that this alone was not sufficient. The molten glass running between the cores congealed before it properly filled the mould. Casting on the open floor had to be abandoned; the mould must be kept hot in a furnace of its own.

§3. CASTING AND ANNEALING THE MIRROR

Before any attempt was made to cast the 200-in. disk, experience was gained with the disks for the smaller auxiliary mirrors for the telescope and for the mirrors to be used in the testing of the 200-inch. Disks progressively increasing in size were cast, the various causes of failure being eliminated in turn. Disks of 30, 60 and 120 inches diameter were cast before the 200-inch disk was attempted, the 120-inch disk being cast in the furnace designed and constructed for the 200-inch.

The cores were made of pieces of the special brick, cemented together, cut down to the correct size and then carefully shaped with a carborundum grinding-wheel. They were fastened down, at first, with a special furnace cement, but broke loose during the casting. The use of cement was therefore abandoned and the cores were anchored with dowels of silica brick. When the 60-inch disk was poured, many of the cores again came adrift; a second attempt was made, the greatest care being taken in the preparation and fixing of the cores. On this occasion one core only broke loose; it was ladled out, the pouring was completed, the disk was annealed for 69 days and a satisfactory disk was obtained, the missing hole where the core had come adrift being drilled out.

It was apparent that failure in the casting of the large disk would be liable to occur if a more secure method of anchoring the cores were not adopted. It was decided to use steel bolts with large heads, the cores being built round the bolts. This meant that the thickness of the cores would be reduced and more care in building them would be required. The 120-inch disk was successfully cast with the cores held down in this way, and a perfect disk was obtained after four months in the annealing oven. This disk had provided a good test of all the arrangements for dealing with the 200-inch disk.

The mould (figure 2) for the 200-inch disk was carried on a heavy circular steel table, to which was fitted a large number of electric heating coils, to keep the disk warm in the annealing oven. Around this was built a special domed or beehive casting oven, of silica brick and cement. The oven was provided with three swing doors to admit the ladles and a number of vents for the escape of the gases. It was maintained at a high temperature with special burners. The annealing oven was built nearby. This was in the form of an insulated steel

tank, just large enough to fit closely over the disk. It was lined inside with a large number of electric heating elements, which may be seen in figure 3, controlled from a special switchboard. The temperature inside the annealing oven could be maintained constant or lowered at any desired rate by suitable adjustment of the current in the heating coils. An automatic control by electric clocks enabled the temperature to be lowered at any desired rate.

On the floor below, a length of wide-gauge railroad was laid and a special truck with small double-flanged wheels, capable of carrying fifty tons, was constructed. It carried a skeleton girder platform, which could be raised or lowered by four powerful screw-jacks, operated by electric motors. After the casting was completed, the disk was to be lowered on to this truck, which was then to be run along the railroad until it was beneath the annealing oven; the disk would then be jacked up until it was safely in the annealer.

The mould for the 200-inch disk was constructed with 114 cores, each fastened to the bottom of the mould by bolts, passing through holes drilled in the steel table, each bolt being fixed in position by a nut working against a spring. Everything was ready for the casting in March 1934. The melting tank, 50 feet long by 15 feet wide, in a furnace heated by gas burners, could hold 65 tons of glass. For ten days before charging commenced, the furnace was heated, in order to raise its temperature to 2700° F. The " batch " for the special Pyrex glass was fed in through a door at one end of the furnace at a rate of 4 tons a day. After it had all melted, it was heated for six days more to ensure uniformity and to allow gas bubbles to escape.

For the ladling process, three overhead monorail tracks were installed, running from the furnace to the three doors of the beehive oven. Each of the three ladles, capable of holding 700 lb. of glass, was suspended by a steel bar from a trolley running along one of the tracks, and was provided with a handle 20 feet long. By means of this arrangement, one ladleful could be taken from the melting furnace and poured into the mould every six minutes. As each ladle was removed from the furnace, the glass hanging round its edge was cleared away with a long bar, and during its transfer to the beehive oven, the outside was cooled by a water spray to prevent it from melting. About 400 pounds of glass were poured into the mould; the remainder, which had solidified on the inside of the ladle, was tipped out into a metal wheelbarrow and returned to the furnace. Ten hours of steady continuous ladling were required to fill the mould, but near the end an unfortunate mischance occurred. The high temperature was too much for some of the bolts and a few of the cores came adrift and floated to the surface of the melt. These were subsequently scooped out; by grinding at the back of the disk, where the cores were missing, the symmetry of the disk could be restored.

It was decided, however, that a second attempt should be made to cast a perfect disk; the imperfect disk would serve to check the conclusions about the length of time required for satisfactory annealing. From a special study in the

laboratory of the annealing properties of the super-Pyrex glass, supplemented by theoretical investigations, it had been concluded that the disk could be perfectly annealed in somewhat less than a year. The imperfect disk was cooled at ten times the safe rate. After thirty days, it was removed from the annealing oven and found to be intact; careful examination by polarized light subsequently showed a slight degree of residual strain and confirmed that the original estimate was a safe one.

Before the second disk was cast, the method of anchoring the cores was modified. After various tests, it was decided to use bolts of chrome nickel steel, which satisfactorily passed a high-temperature test lasting for two weeks. But as an additional precaution against the risk of failure, the cores were made hollow and cool air was drawn through them by a suction fan throughout the process of pouring. The second disk was cast on 2 December 1934, and was completely successful, no hitch occurring during the process. The disk was placed in the annealer, to be maintained at a steady temperature for two months, and then cooled uniformly for eight months more.

But disaster nearly overtook it three months before the annealing was due to be completed. The Chemung River, which flows past the works and is subject to periodical flooding, overflowed its banks and the water rose higher and higher; for the first time in seventeen years it passed the highest safety mark. The annealing oven was out of danger on the second floor, but the transformer and the automatic temperature control equipment were on the ground floor. In spite of all efforts to protect the equipment with sandbags and concrete dykes the water steadily gained, and eventually the current had to be shut off, whilst the transformer and equipment were raised above the danger level. Three days passed before the current could be switched on again. But the dangers were not over, for shortly afterwards Corning was shaken by an earthquake. However, when the oven was opened at the allotted time, the disk was found to be perfect, and careful examination with a polariscope revealed no traces of strain. The disk weighed over $14\frac{1}{2}$ tons. Its cost has not been made public, but the disk was insured by Lloyds of London for $100,000 for its journey across to California.

§4. DELIVERY OF MIRROR TO PASADENA

The disk having been successfully completed, the packing and transport for 3000 miles across the continent to California were not without their problems. The disk was cased in a box made of $\frac{1}{2}$ inch steel plates, with a padding all round of rubber sheeting, also $\frac{1}{2}$-inch in thickness. The disk and casing together weighed 35 tons. It was necessary to transport the disk in the vertical position, as its diameter was too great for carriage by rail or road in the horizontal position. The route was carefully planned and checked, and the heights of all bridges and tunnels where the clearance was small were verified. In places there was not more than an inch or two to spare. A special well-hole car was made to carry the crated disk. Heavy cross-girders bolted to this car supported steel beams,

which had been welded to the disk casing; gum rubber and hardwood blocks, counterbalanced with heavy springs, were placed between the beams on the case and the girders on the car to act as shock absorbers. Steel rods, two inches in thickness, from near the top of the crate to the four corners of the car, tightened by turnbuckles, held the casing firmly in position. Finally, as an additional protection, heavy steel plates were placed at an angle from near the top of the casing to the sides of the car. The speed of the train was limited to 25 miles an hour. The trans-continental journey was completed without incident and the disk arrived at Pasadena on 10 April 1936.

§ 5. THE TELESCOPE AND MOUNTING

Whilst the investigations leading to the casting of the mirror had been under way, progress had been made with the mechanical design of the telescope and mounting. Two fundamental decisions had first to be made. What should be the ratio of the focal length of the mirror to its aperture and what type of mounting for the telescope tube should be adopted? The 100-inch telescope has an aperture ratio of f/5. If the same ratio were adopted for the 200-inch, the focal length would be 83 feet, requiring a very large dome. A shorter focal length would simplify the problems of design, would reduce the size of the dome and would at the same time appreciably reduce the cost. As, moreover, one of the principal applications of the telescope would be to the photography of the faintest and most remote galactic systems, the smaller ratio of focal length to aperture would be advantageous. It was therefore decided to adopt the ratio of f/3·3, giving a principal focal length of 55 feet and requiring a relatively short tube.

The next question to be decided was the type of mounting. A telescope must be provided with two degrees of freedom, so that it can be pointed to any desired part of the sky. Herschel's telescopes and Lord Rosse's 6-ft. reflector had been built so that the two motions were in altitude and azimuth. This type of mounting has the great inconvenience that during observations the telescope must be moved in both co-ordinates to follow the diurnal motion across the sky of the object under observation. More convenient is the equatorial type of mounting, in which the telescope can be turned about an axis (called the polar axis) parallel to the axis of the earth, and about a perpendicular axis (called the declination axis). The advantage of this type of mounting is that, when the telescope has been set on an object, it is only necessary to give it a motion around the polar axis in order to follow the diurnal motion; as, moreover, this rotation is at a uniform rate, it can be carried out mechanically, by clockwork or other suitable means. The invention of the equatorial mounting followed closely that of the telescope itself. Father Scheiner used an equatorial mounting for the heliotrope, with which he made his observations of sunspots, probably as early as 1616, and certainly before 1625, when his *Rosa Ursina*, containing a wood-cut of the heliotrope, was published. He attributed the idea to Father Gruen-berger. The application of a clockwork drive was first made by J. D. Cassini,

Figure 2. Close-up of ceramic mould, showing shape of cores which formed ribbed structure on back surface of disc (Corning Glass Co.).
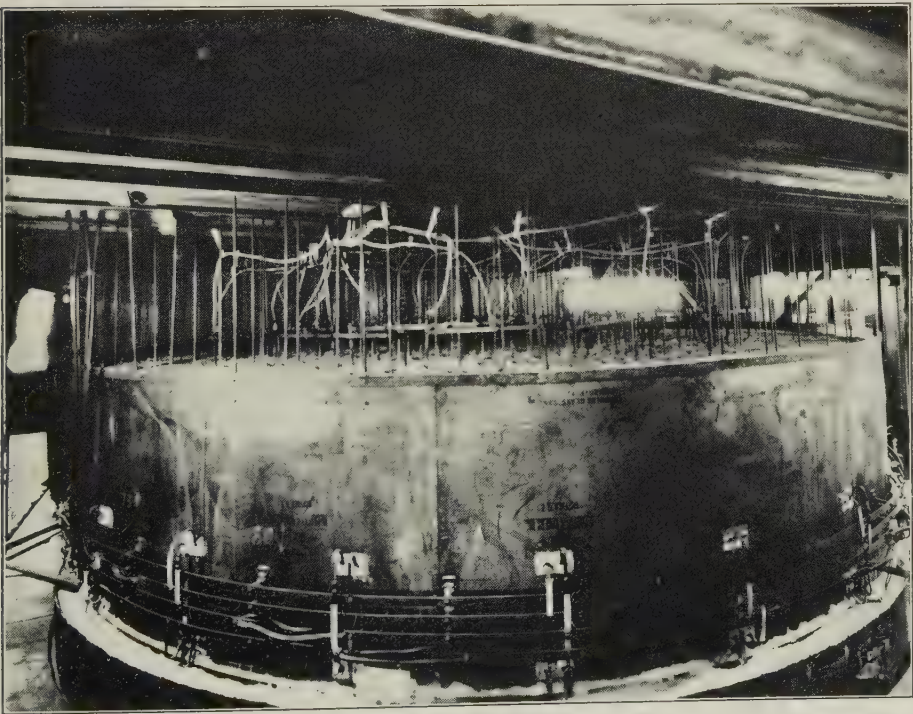
Figure 3. Outside view of annealing kiln, showing heating elements on top (Corning Glass Co.).

Figure 4. 100-inch reflector, Mount Wilson Obervatory.
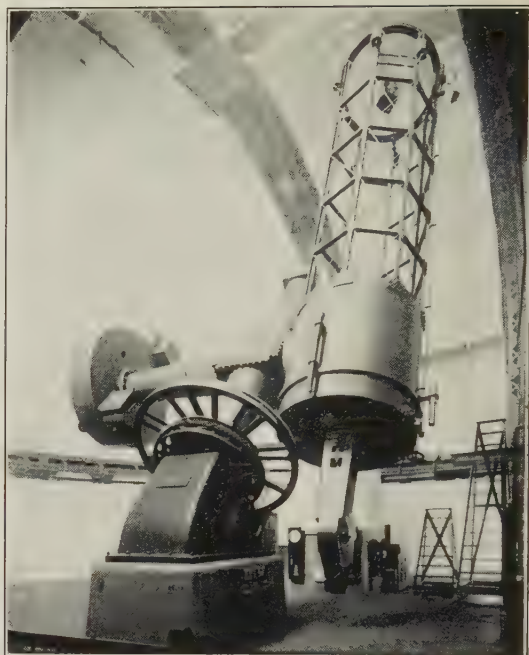
Figure 5. 72-inch reflector, Dominion Astrophysical Observatory, Victoria.
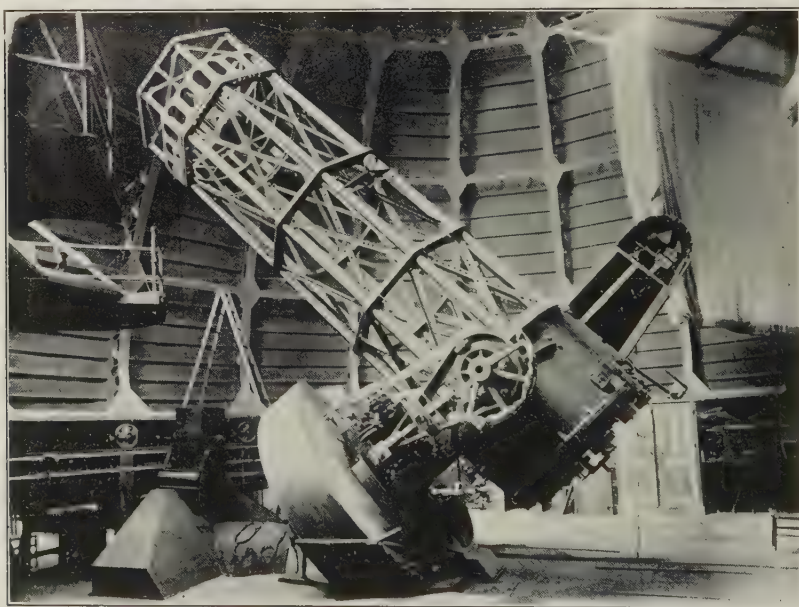
Figure 6. 60-inch reflector, Mount Wilson Observatory.

at the Paris Observatory, somewhere about 1675. The great lengths of the early telescopes, necessitated by the chromatic aberrations of their single-lens objectives, caused the equatorial type of mounting to be abandoned for many years in favour of the altazimuth type. The equatorial mounting is now universally used for large instruments.

Three different forms of this mounting are commonly used. In the *English mounting*, due to Ramsden in 1790, the polar axis is supported at its two ends and is in the form of a yoke within which the short declination axis, carrying the telescope, is mounted. This form of mounting was adopted for the 100-inch reflector at Mount Wilson, shown in figure 4. In the *German mounting*, due to Fraunhofer in 1824, the telescope is mounted at the end of the declination axis, to one side of the polar axis, and a counterpoise weight is placed at the other end of the declination axis, on the opposite side of the polar axis. This mounting is used for the Victoria 72-inch reflector shown in figure 5, and also in the Toronto 74-inch reflector. In the *fork mounting*, first used in Lassell's 2-foot reflector, about 1840, and then in his larger 4-foot reflector, in 1860, a short polar axis carries at its upper end a stiff fork, within which the telescope is hung. The 60-inch reflector of the Mount Wilson Observatory, shown in figure 6, is mounted in this way. The German type of mounting requires a larger dome than the English mounting for housing the same telescope, and the additional weight of the counterpoise has to be supported by the bearings. With the English mounting, on the other hand, there is a region near the north pole where observations are impossible, whereas with the German mounting the telescope can be pointed to any part of the sky. The fork mounting possesses the advantages of both the other types of mounting, without their disadvantages, but unless the latitude of the observatory is high, the overhang of the telescope beyond the upper bearing of the polar axis necessitates a more massive construction and greatly complicates the design.

The design adopted for the 200-inch telescope is an ingenious compromise in which the advantages of both the English and German mountings are retained, but their disadvantages are avoided without the introduction of the other disadvantages of the fork mounting. The mounting is a modification of the English yoke type, the upper bearing being in the form of a large open horseshoe, through the throat of which the telescope can be pointed, enabling observations to be made at the north pole of the sky. The telescope tube, instead of being hung near its lower end, is supported not far below the centre, giving greater stability and making possible a dome of smaller relative diameter than for other large reflectors. The stability of the tube enables the observer to be carried in a cylindrical housing at the principal focus and makes the Newtonian mirror unnecessary. Before any parts of the telescope and mounting were constructed, a complete model on a scale of one-tenth was built and thoroughly tried out.

The telescope " tube " is in the form of a rigid hollow square centre section, with a strong rigid ring at each end. It is seen in figure 7. Each ring is attached

to the central section by eight stiff 20-inch diagonal I beams, forming four triangles whose bases are the sides of the square and whose apices are on the ring, at the ends of two perpendicular diameters. The lower ring carries the mirror and cell, weighing 35 tons; the upper ring carries a cage which supports the housing for the auxiliary mirrors, weighing 30 tons. The bearings, for movement in declination, are carried from two opposite sides of the centre section. The design gives great rigidity and, due to the geometrical construction, the differential flexure is small, the primary and secondary mirrors remaining parallel to one another to a high degree of accuracy. The tube, excluding the mirror cell and upper cage, is 22 feet square, 44 feet long and weighs 75 tons. It was constructed mostly of steel plates, less than one inch thick, welded together, each section being annealed at 1150° F. to relieve strain.

The mirror cell is a cylindrical box of welded steel strongly braced for strength and stiffness. It is nearly 20 feet in diameter and weighs 19 tons. Thirty-six foundation plates for supporting the counterpoised lever arms and ball-bearing mechanisms, by which the mirror is to be supported at its thirty-six cylindrical cells, are mounted on it. It was made by the Babcock and Wilcox Company.

The upper cage, to carry the cylindrical housing, with the auxiliary mirrors and the observer, is 22 feet in diameter and 12 feet high. Because of its size and the impossibility of transporting it by road or rail, a special furnace had to be built for its annealing at the works of the Westinghouse Company at South Philadelphia, on the Delaware River; the same company also received the contract for the tube, yoke and horseshoe.

The largest part of the telescope mounting was the horseshoe-shaped upper bearing. It is the largest bearing ever made, being 46 feet in diameter and 4 feet thick. At the throat it is 12 feet wide, tapering to nothing at the ends. A complicated system of internal bracing gave the necessary stiffness. All the parts were welded together without the employment of a single rivet. The outer bearing rim was made of special steel plate, $4\frac{1}{2}$ inches thick, rolled into segments of a circle in a 10 000-ton armour press. It was made in three pieces because it was necessary to transport it to Pittsburgh for the milling of the bearing face. The only milling machine in the world large enough for this task was the one that had made the giant parts for the Great Boulder Dam, in the Westinghouse plant at Pittsburgh. The design was such that each of the three parts could just be shipped to Pittsburgh through the tunnels in the Allegheny Mountains. The total weight of the horseshoe was about 170 tons, and it contained nearly a mile of welded seams.

Some deformation of the horseshoe as the telescope was turned was unavoidable. It amounted only to one-twentieth of an inch at the tip of its horns; but this would be sufficient to upset the collimation of the mirrors. The effects of this deformation were eliminated by pulling the the horns together with a turnbuckle exerting a tension of 130 tons and inserting a spreader in the throat,

which exerted an outward push of 225 tons. Thus distorted, the bearing surface was milled and polished so as to be truly cylindrical to an accuracy of $0''{\cdot}003$, this task taking 3000 working hours. When the spreader and turnbuckle were removed the horns sprang slightly apart. The effect of deformation as the telescope turns is merely to counteract the distortion thus artifically introduced, the mirrors at the two ends of the tube remaining in perfect collimation.

The thrust bearing at the lower (south) end of the telescope is of the ball and cup type, in the form of a hemispherical shell of steel seven feet in diameter. The upper and lower bearings are connected by the yoke, consisting of two side arms in the form of hollow cylinders, 47 feet long and 10 feet in diameter, made of one-inch steel plates welded together. These arms are attached at their upper ends to the horseshoe and at their lower ends to a cross-piece, in the form of a bent box-girder, 46 feet long and 11 feet deep, which carries the hemispherical bearing, and is stiffened with many internal stiffeners.

The total moving parts of the telescope weigh about 450 tons. In order that the telescope should move smoothly and easily, it was essential that friction at the bearings should be reduced to a minimum. In most modern large telescopes, ball or roller bearings are adequate for this purpose; in the 100-inch telescope a somewhat cumbrous system of mercury flotation is employed, the polar axis having fitted to it at each end a large hollow drum, which floats in a tank of mercury. The large horseshoe bearing of the 200-inch telescope made mercury flotation impracticable; with ball or roller bearings the torque required to turn the telescope would be larger than was desirable, because of the slight deformations of the bearings caused by the great weight resting on them. Both methods were therefore discarded in favour of an oil-flotation system.

The large horseshoe bearing is supported by two oil-pad bearings, each 28 inches square and faced with Babbitt metal, which are mounted on the north pedestal. The hemispherical thrust-bearing at the lower end rests on three oil-pads. Oil is forced through a central hole in each of the pads, under a pressure of 250 pounds. The pressure is sufficient to force the oil outwards from the hole towards the outer edges of the pads, whence it returns to the pump. The telescope thus floats on a film of oil; with roller bearings, a torque of 22 000 pound-feet would have been required to turn the instrument at celestial rate, whereas with the oil-pad bearings a torque of only 50 pound-feet, neglecting the friction of the seals and scrapers, is required.

The rotation in right ascension is applied by two $14\frac{1}{2}$-foot worm wheels mounted below the south bearing. One of these is used for moving the telescope rapidly from one position to another; the other is for driving it at the celestial rate. A worm wheel of similar size on the declination axis is used for moving the telescope in declination. These worm wheels were cut with extreme accuracy in the workshops at Pasadena, in a temperature-controlled room, and the errors of spacing nowhere exceed $0{\cdot}0005$ inch, equivalent to a maximum angular error of about one second of arc.

§ 6. METHOD OF GUIDING THE TELESCOPE

The methods employed for driving and guiding the telescope are of great elaboration. The drive at uniform celestial rate is controlled, in a somewhat complicated manner, by a quartz-crystal oscillator, vibrating at 50 kc., and stepped down by de-multipliers to a frequency of 50 cycles. The apparent celestial motion is not quite uniform, because the true rate is modified by a variety of factors—by changes of refraction due to change of altitude, by the dependence of mean refraction on temperature and barometric height, by small residual errors in the driving gears and by residual flexure effects. The variations caused by refraction can be calculated; the instrumental variations can be determined by observation. Their sum total is obtained mechanically by a " computer ", which consists essentially of a group of cams, differentials and gearing, each of which represents by the position of its shaft a single variation, which can be set up, for the particular object to be observed, by an operator at the control desk. Their combined effect is represented by the position of the master shaft of the computer and is transferred to the drive control by means of an electrical position transmitter. This is of the interlock or Selsyn motor type, such as is used in recording sound for motion pictures.

The driving of the telescope at the desired rate is achieved in the following manner. The telescope is driven by a synchronous motor, controlled through thermionic valves by a variable-frequency string vibrator, in the form of a string carrying a metal weight. The frequency of the vibrator lies between limits of $47\frac{1}{2}$ and $52\frac{1}{2}$ vibrations a second, the variations in frequency being produced by electromagnetic force on the weight, through a potentiometer arrangement. The quartz-crystal oscillator controls a comparison synchronous motor, by its uniform frequency of 50 cycles a second. The clock motor and this comparison motor are compared for angle by a differential. It is required that the output of this differential shall be identical with the output of the computer. The two outputs are therefore compared by another differential; their difference operates the potentiometer or voltage control unit, which controls the frequency of the string vibrator in such a way that any difference is brought to zero. This null method gives a perfectly smooth motion to the telescope in right ascension at precisely the rate required. The movement about the declination axis is controlled by a second computer; in this movement there is no diurnal motion to be taken into account. All that is left to the observer is the correction of the small displacements of the image caused by atmospheric irregularities.

The various control switches are mounted at the control station at the foot of the north pedestal together with the indicators giving the right ascension and declination, the zenith angle of the telescope, the position of the wind-screen, the rates of motion in right ascension and declination, the focus setting, and the sidereal and mean time. The rotation of the dome is automatically controlled by means of a small dummy telescope, which gives the zenith angle; this ensures that the aperture in the dome is always in the direction to which the telescope is pointing. This dummy also automatically controls the position of the wind-

screen. During observations, the next star position to be required is set up on the dials of the master or distributor Selsyn motor. All observing positions are connected by telephone with the control desk. On instructions from the observer to set the telescope to the next star, an " execute " button is pressed; the telescope is automatically moved to the desired position, to an accuracy of five seconds of arc, and the positions of the dome and wind-screen are at the same time adjusted. Each observing station is provided with Selsyn dials, indicating the position of the telescope in right ascension and declination, so that the observer may know that the telescope is set to the required position, with control buttons for guiding the instrument in each co-ordinate, switches for adjusting the focus, and a press button, by means of which everything can be stopped, in case anything jams or goes wrong. Limit switches are provided to limit the motion of the telescope in hour-angle and altitude, as a safeguard against damage to the equipment. It may be mentioned that a total of approximately 100 miles of conductor is used in the electrical control installation.

§7. OPTICAL ARRANGEMENTS

It remains to describe the optical arrangements. The reflecting telescope has the great advantage over the refractor that observations may be made either at the prime focus or, by interposition of suitable hyperboloid mirrors in the converging beam from the mean mirror, longer equivalent focal lengths can be obtained. The 200-inch telescope can be used either at the prime focus, with focal ratio 3·3 and focal length 55 feet, as a Cassegrain combination, with focal ratio 16 and equivalent focal length of 267 feet, or in the Coudé form, with focal ratio 30 and equivalent focal length of 500 feet.

At the upper end of the tube are two six-foot cylinders, each independently supported from the upper cage of the tube. The lower cylinder contains the Cassegrain and Coudé mirrors, together with the mechanisms for swinging them into or out of position. The normal arrangement in large telescopes is for the Newtonian and Cassegrain mirrors each to be mounted in a cage, which can be fixed to the upper end of the tube. When observations require the equivalent focal length to be changed, the complete cage with mirror is changed, which is both troublesome and wasteful of time. In the 200-inch telescope, the auxiliary mirrors when not in use are swung back against the walls of the enclosing cylinder. Either mirror can rapidly be brought by remote electrical control into position for use; appropriate counterpoise arrangements are provided to ensure that the balance of the instrument is not upset. When the mirrors are swung back, the light converges to the photographic plate at the prime focus. The upper cylinder contains an observing chair for the observer; it rests on a circular track and can be rotated and clamped at intervals of $22\frac{1}{2}°$. The plateholder or other apparatus being used is supported from the lower cylinder, and is unaffected by any vibrations caused by movement of the observer. A movable platform, riding on a curved track just below one of the main shutter arches, is provided to enable the observer to get on or off the telescope.

The Cassegrain combination, working at f/16, can be used in two ways. The main Cassegrain focus is just below the central hole, 40 inches in diameter, in the main mirror. At this focus direct photographs can be made with a double-slide plate carrier or spectrographic observations made with a spectrograph with one, two or three prisms. For observations at this focus, the observer sits on a platform supported by telescopic plungers, which is carried on a truck whose wheels may be oriented into any desired position. Instead, however, of converging to this focus, the light can be reflected by a diagonal flat mirror, placed at the intersection of the two axes of the telescope, and thrown through one or other of the hollow declination trunnions into the 10-foot-diameter yoke tube. The flat, measuring $53\frac{1}{2}$ by 40 inches, is supported upon a tube rising through the hole in the main mirror; by remote control it can be rotated around the axis of the tube. When not in use, a crane attached to the inside of the north face of the tube can be brought down to pick up the mirror and deposit it against the tube. Within the yoke tube, an 8-foot plane-grating spectrograph is supported parallel to the polar axis, within a hollow cylinder, and geared so that the slit always remains vertical. There are steps inside the yoke tube, which the observer mounts, making observations at this focus from within the tube. By turning the flat mirror through 180 degrees, observations can be made within the other yoke tube, where a second cylinder is provided to carry a radiometer or any other instrument that must remain vertical.

In the Coudé combination, working at f/30, the converging light reflected from the appropriate Cassegrain mirror falls on the flat mirror at the intersection of the two axes of the telescope. This is adjusted to throw the light along the polar axis through a slot, extending the full length of the south face of the tube, to a focus in a constant-temperature room immediately south of the telescope. The flat mirror is geared to turn in declination at half the rate of the telescope, so that the reflected beam is along the polar axis whatever the position of the telescope. At high declinations the angle of incidence on the flat mirror is unduly large; for observations made at declinations from 50° to the pole, therefore, the position of the flat is adjusted so that it throws the light on to an additional mirror, fixed to the mounting, whence it is reflected to a further mirror on the polar axis and thence to the focus. The constant-temperature room will contain various spectrographs of high dispersion for the detailed study of the spectra of bright objects.

§ 8. ACCESSORIES

In order to extend the usefulness of the 200-inch telescope, some important accessory equipment has been designed for it. A disadvantage of the small focal ratio, when observations are made at the prime focus, is that coma becomes troublesome at a small angular distance from the axis, for the length of the comatic image is directly proportional to the angular distance from the axis and to the square of the ratio of aperture to focal length. At the prime focus of the 200-inch telescope, the effects of coma will begin to be apparent at a distance of about 2′
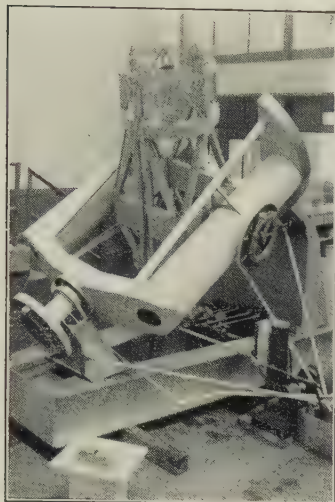
Figure 7 a.   1 : 10 scale model of 200-inch reflector.
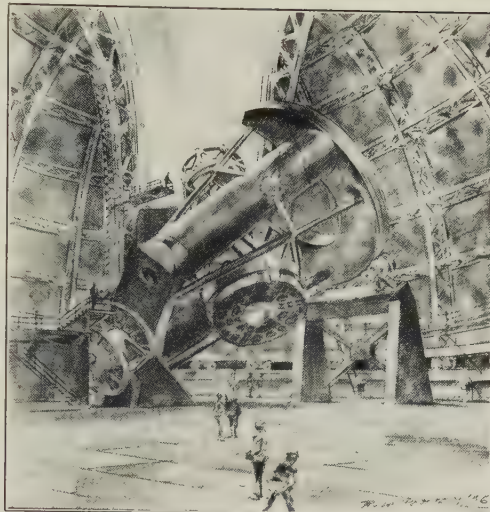
Figure 7 b.   Drawing by R. W. Porter showing general design of mounting.

Figure 8.   Aeroplane view of site for 200-inch reflector on Mount Palomar.

from the axis, so that the total field of good definition is restricted to about 4′. Various modified designs of reflecting telescope have been devised to reduce the effects of coma, the most ingenious being that known as the Schmidt telescope, in which the spherical aberrations, including coma, are corrected by the use of a specially figured correcting lens placed at the centre of curvature of the main mirror, which is spherical, but at the expense of a strongly curved field. For the 60-inch and 100-inch reflectors at the Mount Wilson Observatory, Dr. F. E. Ross had designed special correcting lenses of zero power which, placed near the focus of the mirror, corrected the coma without introducing other aberrations of a serious amount, and greatly increased the field of good definition. For the 200-inch telescope two correcting lenses have been designed. The first of these is intended for use under the best conditions of seeing and will have a spherical aberration confusion disk of 1″·5 diameter; it will increase the area of the field of good definition tenfold. The second is intended for use under average conditions of seeing and will have a spherical aberration confusion disk of 2″·5 diameter; it will increase the area of good definition some twenty- or thirty-fold.

One of the important applications of the 200-inch reflector will be to the study of remote galaxies and the determination of their velocities of recession, from spectra of low dispersion. In order to reduce exposure times for these faint objects as much as possible, special short-focus camera objectives of great relative aperture, combined with good definition, have been designed. The field of view required for this purpose being small, the problem of the design of such lenses is somewhat similar to that of the design of microscope objectives. Dr. W. B. Rayton, of the Bausch and Lomb Optical Company, has designed a lens with an equivalent focus of 32 mm. and a relative aperture of f/0·59, in which the photographic plate is almost in contact with the plane face of the rear component of the lens. This lens was tried with the 100-inch telescope, and showed a great gain in speed over the fastest lens previously obtainable. A lens of even greater speed has been designed by Mr. R. J. Bracey, of the British Scientific Instrument Research Association, and constructed by Messrs. R. and J. Beck, Ltd. It is designed on the principle of the oil-immersion microscope-objective; the focus is on the plane surface of the rear lens of the system, with which the plate is kept in optical contact by a special immersion fluid. The relative aperture of this lens, which will be invaluable for the study of the spectra of faint distant objects, is f/0·35.

Another ingenious accessory is the image-slicer, devised by Dr. I. S. Bowen. In spectroscopic observations, the maximum efficiency of the slit, measured by the fraction of the light forming the image which is passed by the slit, is inversely proportional to the aperture of the telescope and to the focal ratio of the camera lens. With the 200-inch telescope, in stellar observations under good conditions and using a spectrograph of large focal ratio (f/30), the efficiency is only about 5 per cent. Under poor seeing conditions, or when observing non-stellar objects, the efficiency is smaller still. The efficiency is independent of the focal ratio

of the telescope or collimator lens.   The image-slicer is a device by means of which a greatly increased efficiency can be obtained.   The converging beam of light is intercepted, just before it reaches its focus, by a mirror inclined at an angle of 45° to the plane of the slit, and placed near one end and just to the side of the slit.   The beam reflected by this mirror is therefore parallel to the plane of the slit jaws and just grazes their surface.   The mirror is oriented so that the reflected beam crosses the slit at an angle whose sine is the ratio of the width of the slit, b, to the diameter of the image, a.   A series of equidistant small mirrors, whose widths are equal to that of the slit, and which are parallel to the first mirror, intercept the light and reflect it downwards.   The series of mirrors is formed by a stack of aluminized parallel glass plates, each of which extends beyond the previous one by an amount equal to the width of the slit.   If the thickness of each plate is $a\sqrt{2}$, the successive slices of the image are laid down end to end along the slit, forming a continuous line, whose width is equal to that of the slit.   The efficiency is thereby increased to a figure of from 75 to 90 per cent.; this increase in efficiency is obtained not by increasing the intensity of the light at any point of the slit, but by lengthening the portion of the slit that is illuminated and so producing a wider spectrum.   It is customary to widen the spectrum by trailing the star image backwards and forwards along the slit; the image-slicer makes this unnecessary.   But the full gain in efficiency is not in effect obtained, because the spectrum produced by the image-slicer is wider than is required.   The image-slicer is therefore used in conjunction with a cylindrical lens, which is placed in front of the plate with its axis along the direction of the dispersion. The cylindrical lens narrows the spectrum and increases the intensity of illumination on the plate; by the use of suitably designed compound cylindrical lenses of low focal ratio, increases in intensity of illumination by factors of from 10 to 20 can be obtained without introducing harmful aberrations.   The image-slicer is thus a powerful accessory in spectrographic observations.

§ 9. THE DOME BUILDING

The building for housing the telescope has double walls of concrete, with a 12-inch air gap between them.   The interior surface of the inner wall is covered with asbestos insulation.   Around the top of the walls a circular track of two heavy rails was laid, the rails being welded together and ground smooth and level. The dome is supported by a massive ring-girder carried on 32 four-wheeled trucks, which run on this track.   The trucks are fitted with heavy coiled springs.   Horizontal wheels outside and clamps inside prevent the trucks from jumping off the rails.   The outer wheels are larger than the inner, the outer track rail being correspondingly lower.   The skeleton of the dome is formed by two massive box-girder arches, thirty feet apart, which on one side of the dome form the sides of the aperture for observations.   The remainder of the framework is formed of relatively light beams.   The outer covering is formed of steel plates of $\frac{3}{4}$-inch thickness, each weighing one ton, pressed into the correct spherical curvature and butt-welded together, forming a smooth hemispherical structure of great

strength. An inner plating of aluminium panels is fitted, leaving a 12-inch thick air-space. Warm air between the two layers of the dome and the double walls of the building is pumped out from the top of the dome before observations are commenced, cool air being drawn in below. To minimize temperature variations within the dome, the aluminium panels, which form the inner plating, are in the form of hollow boxes of sheet aluminium each filled with crumpled aluminium foil. The dome building is 137 feet in diameter and 135 feet high, and is almost identical in size with the Pantheon at Rome.

The dome is turned by two pairs of 5-H.P. electric motors, with vertical shafts carrying rubber-tyred wheels. These wheels are pressed by springs, under a pressure of several tons, against a smooth welded steel band, a foot wide, laid on edge around the inside of the dome just above the trucks. The tension of the spring is adjusted so as to permit a certain amount of slip at starting while the motors are taking up the load. A smooth easy motion of the dome results and, when the dome is stationary, the pressure of the wheels acts as a brake against wind.

§ 10. SELECTION OF SITE

The choice of a site for a very large telescope requires careful consideration. Unless a site is selected where the conditions are as favourable as can be obtained, the efficiency of the telescope would be greatly reduced and the advantages obtainable from its great light-grasp would in large measure be lost. The requirements are a clear transparent atmosphere, with a low percentage of cloudiness at all seasons of the year; a low daily range in temperature and a moderate annual range in temperature; a high percentage of nights, at all times of the year, when the " seeing " is good, which implies an absence of turbulence; a general freedom from strong winds and remoteness from towns or other sources of artificial light. In addition to these factors, a low latitude is desirable, because this permits observations to extend over the whole of one hemisphere of the sky together with a considerable belt of the other hemisphere; a low latitude has the further advantage that the difference in the length of the nights in winter and summer is less and the duration of twilight is shorter than in a high latitude. There is no site in Great Britain that complies even approximately with these requirements, and the erection of a very large telescope in this country would not be justified. In the mountains of Southern California there are various regions where conditions are very favourable. They are generally good on Mount Wilson, but the scattered light from the artificial lights in the valley below the mountain is sufficient to be troublesome when giving long exposures with fast lenses on faint objects. The general conditions of the whole area were carefully studied; simultaneous tests of seeing were made at a number of selected sites by observers using similar instruments and methods, and measurements of the brightness of the sky were also made.

The site finally selected (figure 8) was on Mount Palomar, in the San Jacinto Mountains, at an altitude of 5600 feet. The mountain is a solid granite block

some 30 miles long and 10 miles wide, lying between two faults, and the risk of trouble from earthquakes is considered to be negligible. It is 125 miles south-east of Pasadena, in a sparsely populated area, where there is unlikely to be trouble from artificial light. On the mountain top a water supply, a Diesel electric power plant, a gas supply, living quarters for the permanent staff and for visiting staff, machine shops and garages have been provided. There are, in fact, all the amenities of life for a small township. Two-way radio communication on a wave-length of $7\frac{1}{2}$ metres is maintained between Palomar and Pasadena. In addition to the 200-inch telescope building, other buildings to house auxiliary instruments have been erected, and an 18-inch Schmidt camera has already been in use for more than three years. A broad motor road with easy gradients up the mountain reaching to the Observatory has been constructed by San Diego County to provide access.

§ 11. CONCLUSION

The 200-inch telescope is nearing completion in the midst of another great war. The optical figuring of the mirror is in an advanced stage, though it would be rash to predict when it will be completed. The final stages of the figuring of a large mirror are apt to be long drawn out, for the polishing heats the mirror, which must be left to acquire a uniform temperature before tests are made on it. As the work nears completion, the proportion of the time spent in waiting for the mirror to settle down and in making tests gets steadily greater. The low co-efficient of expansion of the special Pyrex will here be of distinct advantage. When the mirror is completed, it is intended to coat it with a film of aluminium by the vacuum distillation process in order to secure the advantage of the high reflectivity of aluminium in the ultra-violet, where the reflectivity of silver is low. The construction of a steel chamber large enough to take the 200-inch mirror, and capable of holding a high vacuum of about 10^{-5} mm. of mercury, is one of the many tasks incidental to the completion of this project.

The 200-inch telescope is not only the largest but also the most expensive instrument ever constructed for scientific research. It was made possible by the vision of one man, George Ellery Hale, the greatest of American astronomers; but many have co-operated in working out the details, and its design embodies the ideas of astronomers, physicists, engineers and technicians of all sorts. Much thought and care and toil and skill have gone to its fashioning. The Observatory Council, which has been responsible for the final decision in all questions of design, has not hesitated to depart from hitherto established practice when there appeared to be valid reasons for so doing, and it is safe to assert that the 200-inch telescope will profoundly affect the design of large telescopes in the future. He who would venture to predict what will be discovered with its aid would be rash. But we can be sure that, because it will enable man to probe farther into space than he has yet done, new horizons will be opened up and the question will again be asked what lies beyond. The task of the astronomer will not be ended and the demand for a still larger telescope will once more arise.

THE ACCURATE EVALUATION OF LATTICE SPACINGS FROM BACK-REFLECTION POWDER PHOTOGRAPHS

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ABSTRACT. By considering all the possible systematic errors in the determination of lattice spacings by the back-reflection camera, methods have been devised for their correction. For cubic crystals, if the observed values of lattice spacing are plotted against $\cos \phi$, where ϕ is the supplement of the angle of deviation, a straight line will be obtained. The extrapolation to $\cos \phi = 1$ will give the correct value of the lattice constant. For non-cubic crystals, an analytical method is to be preferred. The systematic errors will make $\cos^2 (\phi/2)$ inaccurate by an amount proportional to $\sin^2 \phi$, which may thus be introduced as a correction term to the Bragg equation in the quadratic form.

Examples of the determination of the lattice spacings of some very pure metals are given. The accuracy attained is about 1 part in 50,000.

§1. INTRODUCTION

IN view of the success of the x-ray method in investigating alloy structures, especially in the determination of solid solubilities, the accurate evaluation of lattice spacings from powder photographs has become of increasing importance and interest, and has been the subject of many investigations. Various types of camera have been designed to suit different purposes. The usual Debye-Scherrer camera as improved by Bradley and Jay (1932) has the advantage that a complete photograph is obtained, while at the same time the lattice spacings may be determined to an accuracy of about 1 part in 30,000. On the other hand, the back-reflection camera is sometimes useful in instances where the specimen should be photographed in the original condition as supplied. It is especially convenient in a metallurgical laboratory, since the ordinary metallographic specimen may be used in conjunction with microscopic examination.

The accuracy claimed in the literature for the determination of lattice spacings by the back-reflection camera seems to be rather optimistic. In view of its wide application it appears worth while to re-examine the whole problem in detail. The present paper aims at a full investigation of all the possible errors in determining lattice spacings by the back-reflection camera and of the methods for their correction. It will be shown that if the errors are corrected by the methods described, lattice spacings may be determined to an accuracy of 1 part in 50,000.

§ 2. SOURCES OF ERROR

In the back-reflection camera used in this laboratory, the specimen to be examined consists of a slab of powder or of a polycrystalline substance placed with its well-planed surface coinciding with the vertical plane through the centre of the camera and perpendicular to the incident beam. The x-ray beam enters the slit system, strikes the specimen, spreads out after diffraction and registers on a cylindrical film wrapped around the circumference of the camera. Our problem is to determine the Bragg angle θ corresponding to each lattice plane (h, k, l) and then to calculate the lattice constants of the crystals composing the specimen.

It is evident that under ideal conditions each line on the photograph should give the same value of the lattice constant, no matter from which plane the line is diffracted. In practice, however, the measured θ is always inaccurate by an amount which itself depends on θ, thus making the measured lattice constant vary with different lines. With regard to the sources of this discrepancy, we are interested here only in the systematic errors, as the accidental errors will be smoothed out by repeated measurements. Among the systematic errors some are due to the imperfection in the construction of the camera, while others are inherent in the process of diffraction. They will be considered separately below.

(a) *The slit system*

By the slit system we mean a collimating tube consisting essentially of two holes at a fixed distance apart. Ideally it should be placed along the X-axis perpendicular to the vertical Y–Z plane containing the specimen. For simplicity let us assume for the time being that the incident beam consists of parallel rays.

Shape of the holes. Our first task is to determine the form of the holes which will yield the true position of the diffracted line. If the incident beam is a geometrical line along XO, then when it impinges on the specimen at O, the diffracted rays will form a cone with vertex at O and semi-vertical angle ϕ, where $\phi = (\pi - 2\theta)$, the axis of the cone being OX. This cone will hereafter be called the standard cone. Corresponding to each angle ϕ, a real slit will give rise to an infinite number of cones, the positions of which are determined by the form and the dimensions of the slit.

We shall prove here that only for a circular hole is the true position of the diffracted line unaffected by the dimensions of the slit. Take a circular hole of radius r. The vertices of the diffraction cones occupy a circular area πr^2 with centre at O in the Y–Z plane, the axes of the cones remaining parallel to OX (figure 1 (a)). It is not difficult to see that all the diffracted rays from the area will be confined within two enveloping cones of the same semi-vertical angle ϕ, with their vertices displaced a distance $r \cot \phi$ from both sides of O along their common axis OX. The pair of enveloping cones and the standard cone are of the same semi-vertical angle, with their vertices lying on the same axis at an equal distance apart. Any circle with centre at O in the X–Y plane will thus cut the

standard cone at two points, each of which is mid-way between the intersections of the enveloping cones with the circle. Therefore, if the position of a line is measured to the middle of its width, the true position as defined by the standard cone is uninfluenced by the dimension of the slit.

The condition is, however, quite different in the case of a rectangular slit. For convenience of comparison let the slit be of width $2r$ and height $2h$, where r is the radius of the corresponding circular hole. Imagine any plane P perpendicular to OX and at a distance D from O. If the hole is circular, the three cones described above will give rise to three concentric circles E, W, E' as shown in figure 1 (*b*). The two enveloping cones intersect the line $L(x=D, z=0)$ at a pair of points I and J. Let a b c d be the projection of the rectangular slit on

(a)   (b)
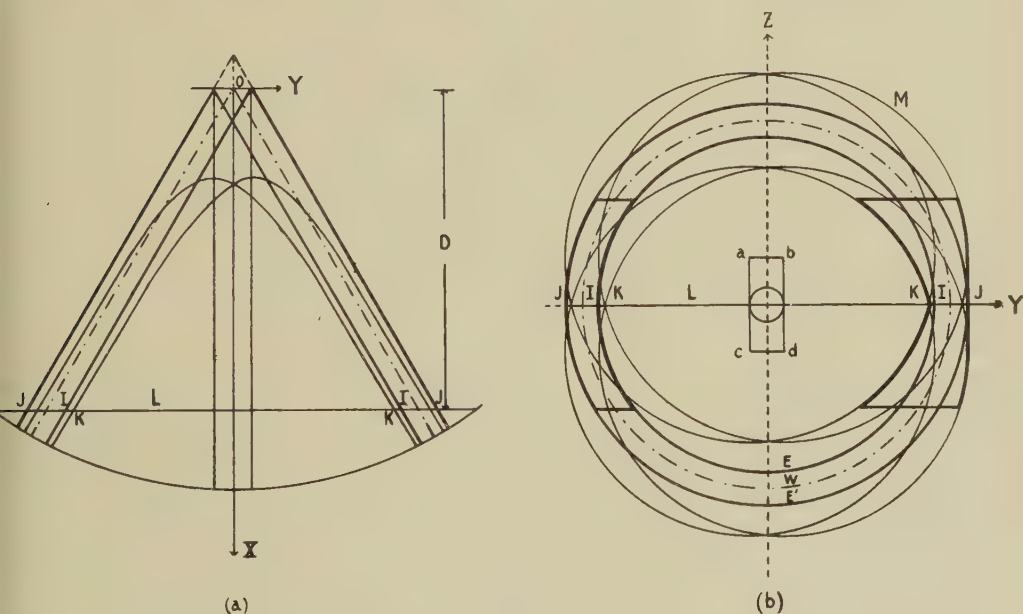
Figure 1.

the plane P. Take b as the centre and $D \tan \phi$ as radius and describe a circle M which is the right section of the cone at a distance D from the vertex b', the projection of the point b on the Y–Z plane. It is clear from the figure that all the lines diffracted from the area a' b' c' d' in the Y–Z plane will intersect the line L at points confined within J and K. In figure 1 (*a*) the two hyperbolas are the sections in the X–Y plane of the cones diffracted from a' b' c' d'. Since KJ > IJ, the measured distance S between a pair of corresponding lines should be less than the true value as defined by the standard cone. This result will still be valid even if the photographic film is wrapped around a cylindrical surface.

We wish to point out here that, besides the above-mentioned advantage, the circular hole has the further merit that the lines are decidedly more regular in

shape than those given by a rectangular slit. In figure 1 (*b*) the heavily lined part at the right side shows the shape of a line obtained with a rectangular slit, while that at the left side shows that obtained with a circular hole.

In the subsequent discussions a circular hole is always assumed.

Inclination of the slit system in the vertical plane. Let the slit system lie in the X–Z plane while inclined at an angle α to the X-axis. In figure 2, AB is the direc-
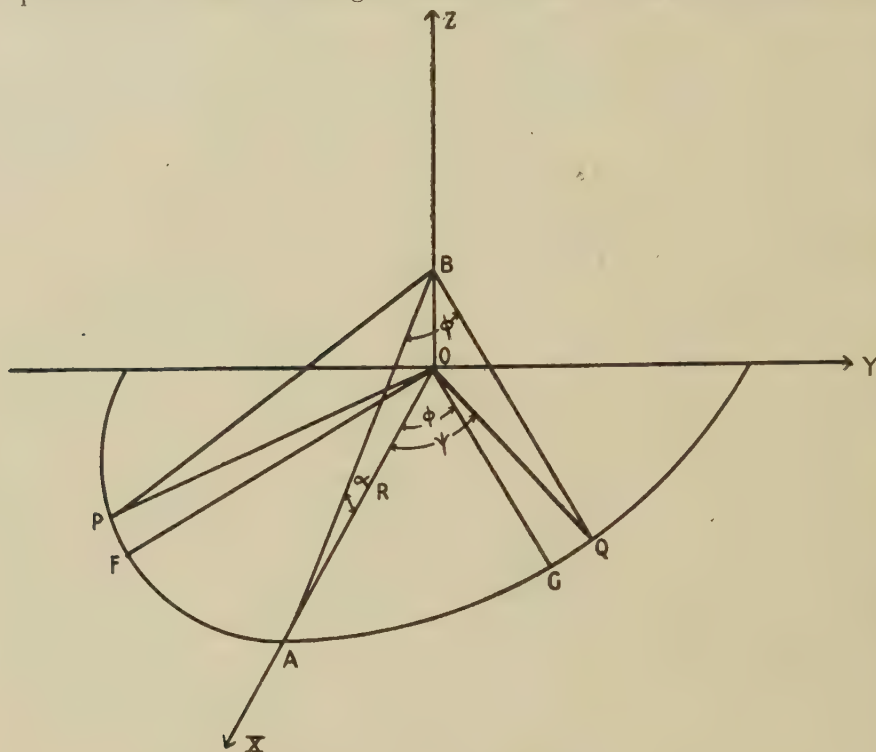
Figure 2.

tion of the incident beam. After the latter impinges on the specimen at B, it gives rise on the cylindrical film of radius R to a pair of lines the positions of which in the X–Y plane are indicated by P and Q. The standard cone gives two points at F and G. If the distance between a pair of corresponding lines is S, we have $\Delta S = 2GQ$.

Now, since
$$AB = BQ = R \sec \alpha,$$
$$AO = QO = R;$$
$$\therefore \quad AQ^2 = 2R^2 \sec^2 \alpha (1 - \cos \phi) = 2R^2(1 - \cos \psi),$$
where ψ is the angle between OA and OQ. So

$$\Delta S = 2R\{\cos^{-1}[1 - (1 - \cos \phi) \sec^2 \alpha] - \phi\} \simeq 2R \frac{\sin \phi}{1 + \cos \phi} \alpha^2. \quad \ldots\ldots(1)$$

This shows that the measured S is always greater than its true value. As ΔS tends toward zero with ϕ, the inclination of the slit system in the vertical plane

is not considered a serious defect, as will be clear from later discussions. In practice, if α is less than 2°, a condition which is readily fulfilled, the error stated in (1) is vanishingly small and may be neglected.

Inclination of the slit system in the horizontal plane. Next let us consider only the X–Y plane. Let the incident beam be AO′, which makes an angle β with the X-axis and intersects the Y-axis at a distance m from the origin (figure 3). Corresponding to any definite angle ϕ, the beam produces two points P and Q
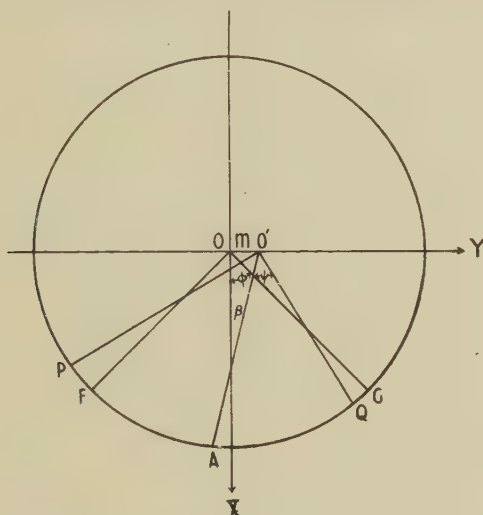
Figure 3.

on the film. As before, F and G are the two points which should be produced by the standard cone. One notices in the figure that the inclination of the slit system in the horizontal plane will in the first place make the pairs of lines asymmetrical with respect to the X-axis. In the second place it causes an error $\Delta S = PF - QG$.

The equations for the straight lines O′P and O′Q are

$$\text{O′P}: \quad y + x \tan(\phi + \beta) = m,$$
$$\text{O′Q}: \quad y - x \tan(\phi - \beta) = m.$$

Then, with the coordinates of F and G known, the distance PF and QG may be written approximately as

$$PF = R \sin \beta - m \cos(\phi + \beta),$$
$$QG = R \sin \beta - m \cos(\phi - \beta),$$

since β is usually very small. This gives

$$\Delta S = 2m \sin \beta \sin \phi. \qquad \ldots\ldots(2)$$

(b) *Divergence of the incident beam*

Let us assume that the incident beam has a circular divergence of semi-divergence angle ξ. If the radius of the slit is r and the two slits are separated

by a distance $2l$, then the maximum divergence is given by $\xi = \tan^{-1}(r/l)$. As the slit system is circular, we have to consider only the X–Y plane.

Let the vertex of the divergence cone be located at V, where $OV = n$. It is clear from figure 4 that the divergence of the incident beam broadens the diffracted line asymmetrically with respect to the proper position defined by the standard cone. The error caused in S is $\Delta S = GQ - PG$.
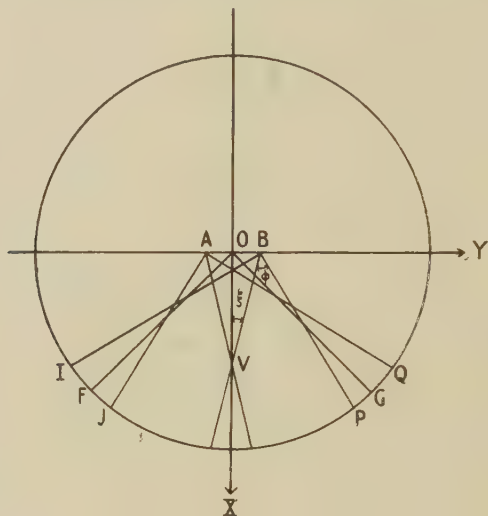
Figure 4.

In figure 4 the equations for the lines BP and AQ are

$$BP: \quad -x \tan(\phi - \xi) + y = n \tan \xi,$$
$$AQ: \quad x \tan(\phi + \xi) - y = n \tan \xi.$$

If ξ is small, GQ and PG may be taken approximately as the distance of the point G to the lines AQ and BP. Thus

$$GQ = R \sin \xi - n \tan \xi \cos(\phi + \xi),$$
$$PG = R \sin \xi - n \tan \xi \cos(\phi - \xi).$$

Consequently $$\Delta S = 2n \tan \xi \sin \xi \sin \phi. \qquad \ldots\ldots(3)$$

(c) *Displacement of the specimen*

In order to avoid spottiness of the diffracted lines, the specimen is kept rotating during the exposure. The region of the specimen effective for diffraction is regulated by the eccentricity of the rotating axis, which is perpendicular to the specimen. It is clear that so long as the rotating axis remains parallel to the X-axis and the specimen lies in the Y–Z plane, the eccentricity causes no error in the measured distance S. Even if the specimen is inclined to the rotating axis, the only effect is to broaden the line symmetrically on both sides of the correct position, producing thus no real error. The condition is, however, quite different if the

rotating axis is inclined to the X-axis.   In this case, the distance S will be shortened or lengthened according to the direction of the inclination.   One may see that this is equivalent to the forward or backward displacement of the speci-men along the X-axis with respect to the Y–Z plane.   Consequently they will be considered together, as follows.
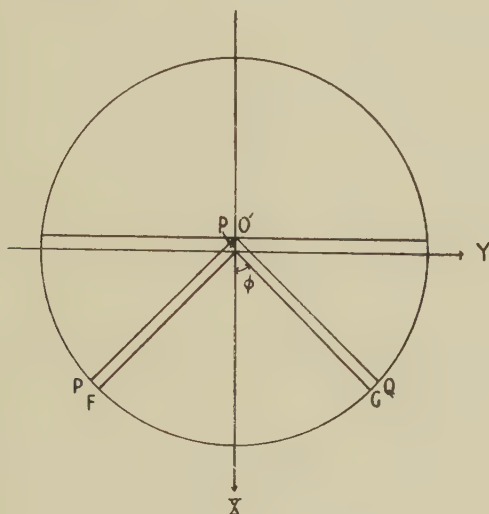
Figure 5.

In figure 5 let p be the displacement of the specimen.   P, Q are two points produced by the displaced cone of semi-vertical angle ϕ, while F, G are two points given by the standard cone.   Since GQ is approximately equal to the normal from G to O′Q, we may write

$$\Delta S = 2p \sin \phi,$$
.....(4)

which is the error caused in S.

(d) *Penetration of the incident beam into the specimen*

X-rays penetrate to a certain depth of the specimen, depending on the absorp-tion coefficient of the specimen for these rays.   Except in the case of very strong absorption, the penetration of the incident beam will widen the diffracted line appreciably toward its outer edge, thus increasing S.   The measurement of the exact position of the line is complicated by the fact that the line is of varying in-tensity, decreasing from the inner edge toward the outer edge.   Assuming that the measurement is made to the centre of gravity of the line, the error ΔS may be calculated in the following way :—

As shown in figure 5, at a depth of penetration p the path of x-rays in the specimen is $p(1 + \sec \phi)$.   After emergence, the intensity becomes

$$I_p = I_0 Q e^{-\mu p(1 + \sec \phi)},$$

where I_0 is the intensity of the incident beam, Q is a factor depending on ϕ, and μ is the effective linear absorption-coefficient of the specimen.

For mathematical convenience, we shall consider p as extending to infinity. If the position of the centre of gravity C is measured from the point G where the standard cone intersects the circumference of the film in the X–Y plane, we have

$$GC = \int_0^\infty p \sin \phi I_p dp \Big/ \int_0^\infty I_p dp$$

$$= \sin \phi / \mu (1 + \sec \phi).$$

It follows that $\qquad\qquad \Delta S = 2 \sin \phi / \mu (1 + \sec \phi).$ $\qquad\qquad$ .....(5)

(e) Film shrinkage

The angle ϕ is obtained by measuring the distance S between a pair of corresponding lines. If ϕ is expressed in radians,

$$S = 2R\phi,$$

where R is the effective radius of the camera. In actual cases the effective radius varies with each photograph, depending on the thickness of the film and the amount of subsequent shrinkage. To account for this uncertainty, Bradley and Jay (1932) have proposed for the Debye-Scherrer camera that two knife edges should be provided, the shadows of which would serve as two permanent points of reference. In this way, the uncertain value of the effective radius is replaced by a fixed angle which is not influenced by the factors mentioned above, and film shrinkage is automatically accounted for. Thus

$$S/\phi = S_k/\phi_k,$$ $\qquad\qquad$ .....(6)

where S_k is the distance on the photograph between the two knife edges and ϕ_k is the corresponding fixed angle.

Although the method of using a fixed angle has been criticized by others (for instance, Buergers, 1937) on the ground that it requires the exact knowledge of a standard lattice-spacing in calibration, yet if the fixed angle is determined by calibrating against the geometrical constant 2π, the method becomes absolute. As this method is very convenient, and may be applied to any circular camera, it will be published elsewhere in detail.

In this connection we have considered the idea suggested by Cohen (1936) and others that the back-reflection camera is inherently precise in the sense that any shrinkage correction tends toward zero with ϕ. In order to retain the linearity of the extrapolation curve which will be described later, we are, however, inclined to think that the fixed-angle method should be adopted.

§ 3. METHODS OF FINDING LATTICE SPACINGS

We have shown that all systematic errors in S may be combined in a single equation,

$$\Delta S = 2[m \sin \beta + n \tan \xi \sin \xi + p + 1/\mu(1 + \sec \phi)] \sin \phi, \qquad \text{.....(7)}$$

with $\sin \phi$ as a common factor. In practice, this may be written approximately

$$\Delta S = 2K \sin \phi. \qquad \ldots\ldots(8)$$
$$S = 2R\phi,$$

so

$$\Delta\phi = (K/R) \sin \phi. \qquad \ldots\ldots(9)$$

Now for every lattice plane of spacing d, Bragg's law states that

$$2d \cos (\phi/2) = n\lambda. \qquad \ldots\ldots(10)$$

Assuming that there is no error in λ,

$$\Delta d/d = (1/2) \tan (\phi/2)\Delta\phi. \qquad \ldots\ldots(11)$$

Combining with (9), we obtain finally

$$\Delta d/d = (K/2R)(1 - \cos \phi). \qquad \ldots\ldots(12)$$

This is also equal to $\Delta a/a$ for cubic crystals, a being the lattice constant.
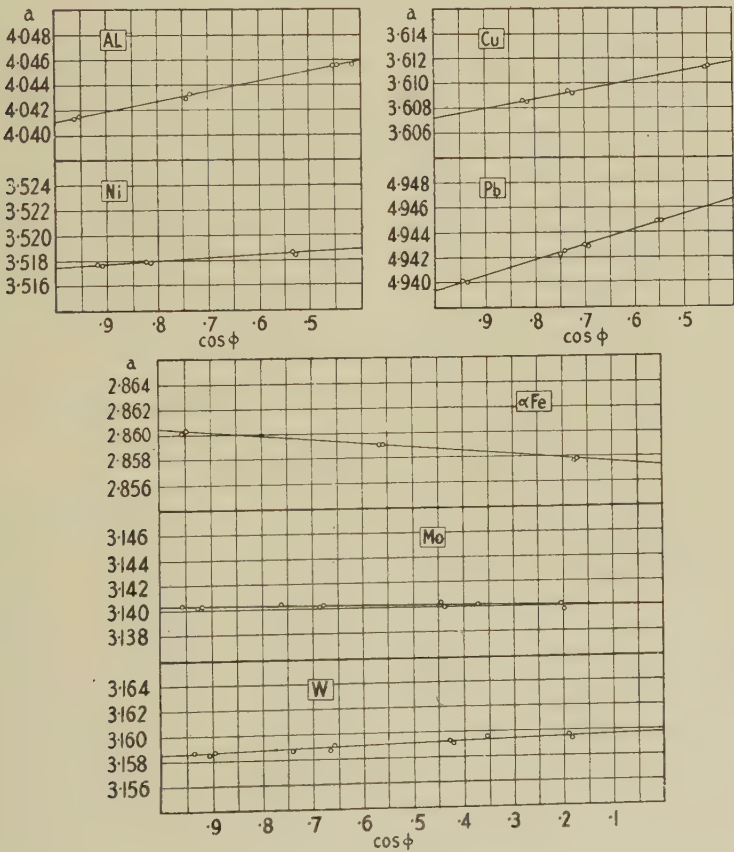
Figure 7.

This shows that for cubic crystals, if the observed values of lattice spacings are plotted against $\cos \phi$, an approximate straight line will be obtained. The extrapolation to $\cos \phi = 1$ should give the correct value of a.

For non-cubic crystals, any graphical method appears impracticable, if not impossible. Here some form of analytic method is to be preferred. In view of the fact that it is difficult to assign definite weights to individual observations, and that the number of lines in a film is usually insufficient to warrant the compliance of the accidental errors with the theory of probabilities, the method of least squares as suggested by Cohen (1935) should be applied with caution.

Take hexagonal crystals as an example. The quadratic form expressed in

Table 1. Cadmium

h k l	Radiation	$\cos^2(\phi/2)$ (obs.)	$\delta \sin^2 \phi$	$\cos^2(\phi/2)$ (corr.)	$\cos^2(\phi/2)$ (calc.)
2 1 1	Cu Kα_1	0·64061	0·00246	0·64307	0·64285
2 1 1	α_2	0·64340	0·00245	0·64585	0·64607
2 1 2	α_1	0·69724	0·00226	0·69950	0·69927
2 1 2	α_2	0·70044	0·00224	0·70286	0·70277
2 1 3	α_1	0·79153	0·00176	0·79329	0·79330
2 1 3	α_2	0·79554	0·00174	0·79728	0·79727
3 0 0	α_1	0·80045	0·00171	0·80216	0·80235
3 0 0	α_2	0·80461	0·00168	0·80629	0·80635
2 0 5	α_1	0·82539	0·00154	0·82693	0·82675
2 0 5	α_2	0·82934	0·00151	0·83085	0·83088
3 0 2	α_1	0·87640	0·00116	0·87756	0·87757
3 0 2	α_2	0·88077	0·00112	0·88189	0·88196
2 1 4	α_1	0·92418	0·00075	0·92493	0·92494
2 1 4	α_2	0·92889	0·00071	0·92960	0·92956
1 1 6	α_1	0·94390	0·00057	0·94447	0·94447
1 1 6	α_2	0·94850	0·00052	0·94902	0·94919

Table 2. Antimony

h k l	Radiation	$\cos^2(\phi/2)$ (obs.)	$\delta \sin^2 \phi$	$\cos^2(\phi/2)$ (corr.)	$\cos^2(\phi/2)$ (calc.)
$\bar{2}$ 2 2	Cu Kα_1	0·70098	0·00044	0·70054	0·70063
$\bar{2}$ 2 2	α_2	0·70496	0·00044	0·70452	0·70413
3 5 3	α_1	0·73576	0·00041	0·73535	0·73538
3 5 3	α_2	0·73934	0·00041	0·73893	0·73906
0 4 3	α_1	0·78320	0·00036	0·78284	0·78288
0 4 3	α_2	0·78702	0·00035	0·78667	0·78676
1 5 2	α_1	0·85314	0·00026	0·85288	0·85287
1 5 2	α_2	0·85744	0·00026	0·85718	0·85714
2 5 4	α_1	0·86349	0·00025	0·86324	0·86324
2 5 4	α_2	0·86785	0·00024	0·86761	0·86756
$\bar{1}$ 4 1	α_1	0·88507	0·00021	0·88486	0·88451
$\bar{1}$ 4 1	α_2	0·88948	0·00021	0·88927	0·88894
$\bar{2}$ 3 $\bar{1}$	α_1	0·89526	0·00020	0·89506	0·89506
$\bar{2}$ 3 $\bar{1}$	α_2	0·89967	0·00019	0·89948	0·89954
3 5 5	α_1	0·95945	0·00008	0·95937	0·95946

terms of ϕ can be written as

$$\cos^2 \phi/2 = (h^2 + k^2 + hk)A + l^2 C,$$

where $A = \lambda^2/3a^2$, $C = \lambda^2/4c^2$, a and c being the lattice constants. From equation (12) we can prove that the systematic errors will render $\cos^2 (\phi/2)$ inaccurate by

Table 3

Sub-stance	Sample	Temp. (°c.)	Lattice constant (A.)	Probable error	Reference
Al	Aluminium Française 99·992 %	20	4·0411	0·0001	Authors
		18	4·0406	0·0002	Owen and Yates, 1936
		25	4·04143	0·00002	Ievinš and Straumanis, 1933
		25	4·0413$_9$	0·0000$_8$	Jette and Foote, 1935
		20	4·040(2)	—	Neuburger, 1933
α-Fe	Hilger H. S. brand (8038) 99·96 %	20	2·8605	0·0001	Authors
		—	2·8605	—	Bradley and Jay, 1932
		25	2·8604$_6$	—	Jette and Foote, 1935
		18	2·8607	0·0002	Owen and Yates, 1933
Ni	Hilger H. S. brand (7636) 99·971 %	21	3·5174	—	Authors
		—	3·5170	—	Bradley and Jay, 1932
		18	3·5172$_4$	—	Owen and Yates, 1936
		25	3·5168$_4$	0·0000$_8$	Jette and Foote, 1935
Cu	Hilger H. S. brand (10300) 99·999 %	19	3·6072	—	Authors
		18	3·6077	0·000$_2$	Owen and Yates, 1933
		—	3·607	—	Lange, 1925
Mo	Hilger H. S. brand (6422)	20	3·1403	—	Authors
		—	3·140$_3$	0·001	Owen and Iball, 1932
		25	3·1410$_3$	0·0000$_4$	Jette and Foote, 1935
W	Hilger H.S. brand (6/02/A3216)	21	3·1585	—	Authors
		—	3·159$_3$	0·001	Owen and Iball, 1932
		25	3·1583$_7$	0·0001	Jette and Foote, 1935
		—	3·1588	—	Moeller, 1937
Pb	Hilger H. S. brand (11.116)	21	4·9394	0·0001	Authors
		18	4·9396	0·0003	Owen and Yates, 1933
		20	4·9389	—	Neuburger, 1933

Sub-stance	Sample	Temp. (°c.)	a	c	c/a	Reference
Cd	Hilger H. S. brand (10547) 99·9999 %	21	2·972(8)	5·605(4)	1·885(6)	Authors
		20	2·973(6)	5·605(8)	1·885(2)	Stenzel and Weerts, 1932
		25	2·9731$_1$	5·6069$_4$	1·88588	Jette and Foote, 1935
			±0·0001$_4$	±0·0004$_5$	±0·0002$_4$	—
		18	2·9723$_8$	5·6038$_8$	1·8853$_2$	Owen and Roberts, 1936
Sb	Kahlbaum Special	22	4·497(2)	($\alpha = 57°\ 6'\ (37'')$)		Authors
		25	4·4976$_2$ ±0·0001$_8$	($\alpha = 57°\ 6'\ 27'' \pm 19''$)		Jette and Foote, 1935

an amount proportional to $\sin^2 \phi$.   Therefore for every line measured we have

$$\cos^2 (\phi/2) + \delta \sin^2 \phi = (h^2 + k^2 + hk)A + l^2C, \qquad \ldots\ldots(13)$$

where δ is the *drift constant*, the sign and magnitude of which may differ with different photographs.

An alternative to the method of least squares is to select three $K\alpha$ lines from the resolved doublets which can be measured with accuracy.   The solution of three simultaneous equations such as (13) will then suffice to yield the true values of a and c together with δ.   A final comparison of the calculated and the observed values of $\cos^2 (\phi/2)$ of all the lines measured will serve to check the calculation.

§ 4. EXAMPLES

Examples will be given of the determination of lattice constants of some very pure metals by a camera of radius approximately 4·5 cm.   In order to obtain the best results, the samples were first reduced to fine powder and then heat-treated at temperatures adequate to remove cold work.   Figure 6 shows the x-ray photographs of the cubic crystals.   Except Fe, which was taken with Co radiation, they were all taken with Cu radiation.*   The extrapolation curves are shown in figure 7.   In each case the experimental points are found to lie very closely on a straight line, thereby giving evidence of the validity of equation (12). In view of the fact that the linearity of the extrapolation curve holds only for large values of θ in the case of Debye-Scherrer cameras, we are inclined to think that by using the extrapolation described method above, the back-reflection camera should yield more consistent results than those obtained with the Debye-Scherrer camera.   For non-cubic crystals, the calculated values of $\cos^2 (\phi/2)$ and those observed and then corrected are shown in tables 1 and 2 to agree satisfactorily.

Throughout the entire calculation, Siegbahn's values of wave-lengths are used.   No correction has been made for the deviation from the Bragg law due to refraction.   Table 3 gives the comparison between the lattice constants determined by the present authors and those by others.

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* Some lines due to W Lα radiation are also present.
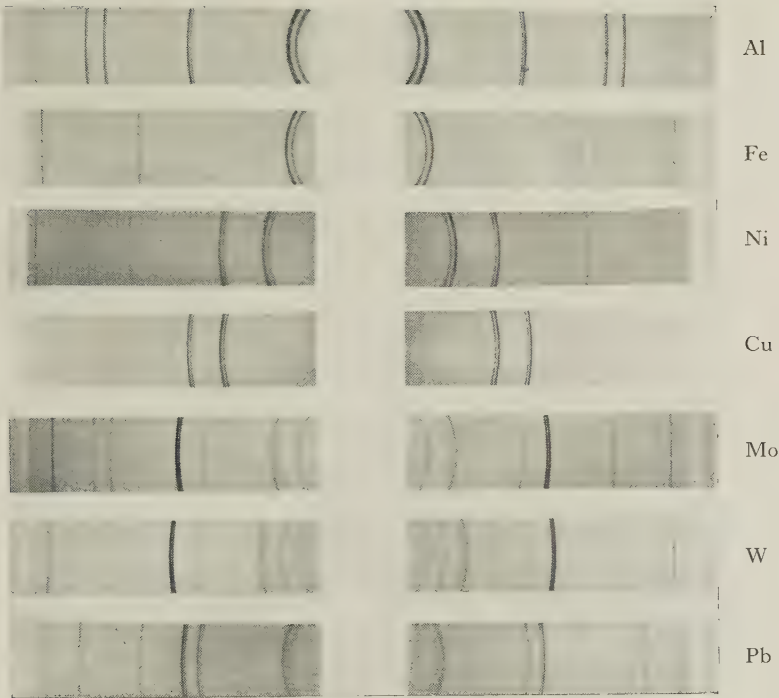
Figure 6.

Figure 1. (111) reflection from small diamond ; FeKα radiation ; surrounded by " paper " diffraction rings ; film normal to reflected beam.

Figure 2. (11ī) reflection from larger diamond ; FeKα radiation ; showing " paper " diffraction conics ; film normal to incident beam.
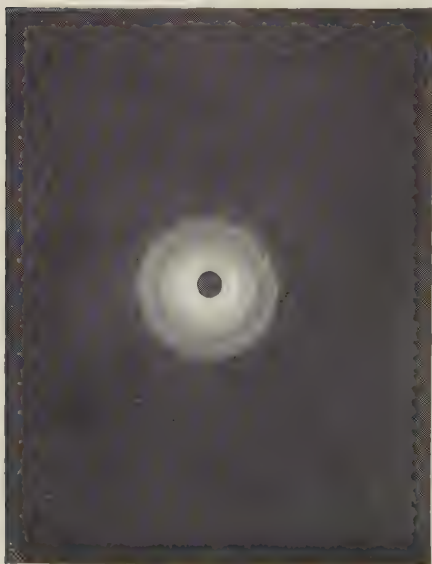
Figure 3. Diffraction pattern due to black paper alone ; direct beam from Fe anti-cathode ; film normal to incident beam ; distance 2·27 cm.
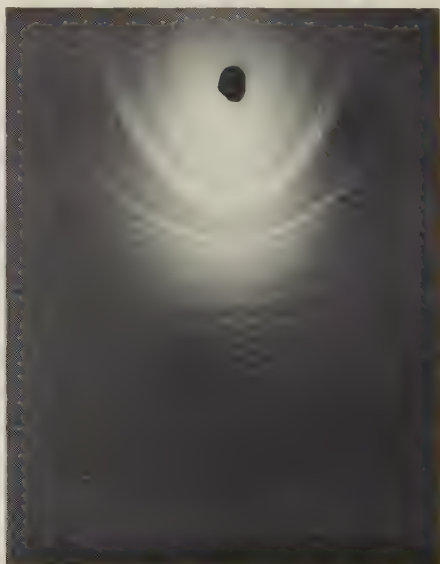
Figure 4. Diffraction pattern due to black paper when normal to film makes angle of 56° with incident beam ; distance 2·5 cm.

A SECONDARY DIFFRACTION EFFECT ON LAUE PHOTOGRAPHS OF DIAMOND

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ABSTRACT. Using a normal arrangement of apparatus, and x rays from a Cu or Fe target, well-exposed Laue photographs of diamond sometimes show sharp diffraction curves around (111), (220) or (113) Laue spots. These curves are due to secondary diffraction by the black paper (light-tight) cover of the film-holder, and they only occur when the crystal is correctly set, to within $\pm 0°·3$, for selective reflection of the characteristic $K\alpha$ or β radiation from one of these strongly reflecting diamond planes. This effect is a useful indication of correct crystal setting for monochromatization, and it also provides a measure of the width of the monochromatized beam. This secondary diffraction may introduce error in connection with intensity measurements, especially when long wave-length radiation has been used.

WHILST taking Laue photographs of various diamonds, using radiation from an iron anticathode of the 5 kw. tube at the Davy Faraday laboratory, it was observed that when the crystal setting was just right for selective (111) reflection of FeKα radiation, the (111) Laue spot was surrounded by a number of beautifully sharp diffraction curves. These curves, which later were proved to be due to secondary diffraction by the black paper covering the film-holder, were conic sections having the (111) spot as one focus when the plane film-holder was perpendicular to the incident beam (figure 2), circles when the film-holder was perpendicular to the reflected beam (figure 1). In favourable cases as many as six or more curves could be seen, the second and fourth (in order of increasing size) being apparently the most intense. Similar curves were subsequently found about the (111) FeKβ Laue spot and the (220) and (113) FeKα spots, and have also been observed with Cu radiation.

In order to ascertain the origin of these curves, which was at first obscure, a number of experiments were carried out, altering different variables of the apparatus; these yielded some results interesting from a more general experimental point of view.

It was the fact that the diameter of the curves did not vary with crystal-to-film distance, over a range of 2·5 to 9·5 cm., that led to their identification. Slight variations did occur, even in experiments intended to be exact duplicates, but these were due to the difficulty of replacing the film in the holder so that the

black-paper-to-film distance was constant. Deliberate variation in this distance by means of stops produced a corresponding variation in the dimensions of the diffraction curves. A direct photograph of a small piece of black paper showed powder rings (figure 3) which for a 10-minute exposure were surprisingly strong. The dimensions and intensities of these rings agree, allowance being made for the heterogeneity of the direct beam and different paper-to-film distance, with those observed on the diamond photograph (figure 1). If the photographic film is set obliquely to the incident beam, the powder rings given by the black paper appear as conics on the photograph (figure 4). The black paper, which is usually cut from an ordinary film envelope, is an indispensable part of the x-ray equipment; its powder photograph is practically identical with that of filter paper, that is, of pure cellulose.

The appearance of the curves on the Laue photographs was found to be sharply dependent upon the accuracy of the diamond setting. The curves disappeared when the crystal was turned through $\pm 0°\cdot3$ on either side of the exact position for $FeK\alpha$ selective reflection and were noticeably weaker at only $\pm 0°\cdot1$ from the exact Bragg angle. Their intensity was also diminished almost to vanishing point when the incident beam passed entirely *through* the crystal (even though the exposure was increased so as to give an exceptionally strong Laue photograph), but reached a maximum when selective reflection took place entirely at a crystal face. These conditions are related to the efficiency of the diamond as a monochromator.* The incident beam is slightly divergent, and the (111) and other Laue spots increase in size as the crystal-to-film distance increases. The sharpness of the paper diffraction curves does not, however, vary with distance to any noticeable extent. The fact that the curves disappear when the diamond crystal is turned through $\pm 0°\cdot3$ on either side of the exact Bragg angle shows that this is the extent of the most intense part of the beam reflected from the (111) plane. The diamond surface is known from electron-diffraction experiments to be plane to within a few minutes of arc.

Iron radiation is strongly absorbed even by carbon, and after its passage *through* the crystal, the reflected beam contains very little radiation of wave-length 1·93 A., although there is still plenty of short-wave-length radiation giving a strong Laue photograph. In particular, there will be sufficient radiation of wave-length 1·93/3 to give a strong (333) reflection in the (hhh) Laue position, while higher orders may also be present. After reflection through the diamond, therefore, the Laue photograph appears just as intense as when reflection takes place off the face, but the " paper " curves, since they are due to the FeK radiation, are very weak or absent in the former case. In the same way, a short-exposure photograph of the main (undeflected) beam shows no paper rings when the

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* Note added 17. 7. 1941. " Transparent " (type II) diamonds give much more intense paper curves than normal (type I) diamonds. The reflected beams from the former can easily be seen on a fluorescent screen in broad daylight. We have also observed excellent paper curves on a Laue photograph of NaCl.

beam has passed entirely through the crystal, but shows the rings when the diamond has been removed, although they are naturally not as sharp as those due to the secondary diffraction of the monochromatized radiation.

Measurement of the intensity of x-ray reflection depends for its accuracy upon a correct estimation of " background ". Our increasing knowledge of the diffuse scattering which accompanies each reflection has introduced to us one serious complication in the measurement of " background " intensity. The existence of these " paper " diffraction curves, whose shape varies with their position on the film, further complicates the process of accurate intensity measurement. The dissipation of the reflected radiation by backward scattering, whether from the light-tight covering of a film or plate or from the window of an ionization chamber, may also prove a source of error, especially in the case of long wavelength radiation.

On the other hand, the " paper " curves are a useful test of monochromatization. We have occasionally required some quick method of determining whether the diamond (which was being used for observation of " diffuse reflections ") was exactly in the position for selective reflection of FeKα radiation by a given plane. The presence of strong " paper " curves surrounding the corresponding Laue spot was an absolute proof that the setting was correct to within $\pm 0°\cdot1$.

The various diamonds used in these experiments were kindly lent to us by Professor W. T. Gordon.

SPHERICAL ABERRATION IN OPTICAL SYSTEMS

By Instructor-Captain T. Y. BAKER, R.N. (Ret.)

ABSTRACT. The paper deals with the shapes of caustics when aberrations of higher order than the first are taken into account. It is shown that, where a system is under-corrected at the " zone ", it should be substantially under-corrected at the edge in order to obtain the best performance.

P ROVIDED all the rays proceeding from an object point on the axis of an optical system make only small angles with that axis, they will emerge through an image point at a position calculated from the paraxial formulae. Rays making finite angles with the axis will, however, be subjected to aberration, and it is the task of the optical designer to keep these aberrations as low as possible by suitable choice of the number, positions and curvatures of his refracting surfaces, as well as the types of glass used.

·T. Y. Baker

In figure 1 let I be the paraxial image point and let a ray which emerges so as to make an angle $\tan^{-1} t$ with the axis cut that axis at a point I'. The distance I'I is known as the longitudinal spherical aberration of the ray, and it can be expressed as $At^2 - Bt^4 + \ldots$, where At^2 is commonly known as the first-order spherical ; Bt^4 is second-order, and so on. If we neglect everything beyond the first-order term, the equation of the ray is $y = tx - At^3$, and this ray will touch the semi-cubical parabola $27Ay^2 = 4x^3$ at the point $(3At^2, 4At^3)$. The ray cuts the caustic again at the point $C'(\frac{3}{4}At^2, -\frac{1}{4}At^3)$. If t is the slope of the steepest ray that contributes to the image formation, the radius of the image patch on the focal plane through the paraxial focus is At^3, but if the image be received on the
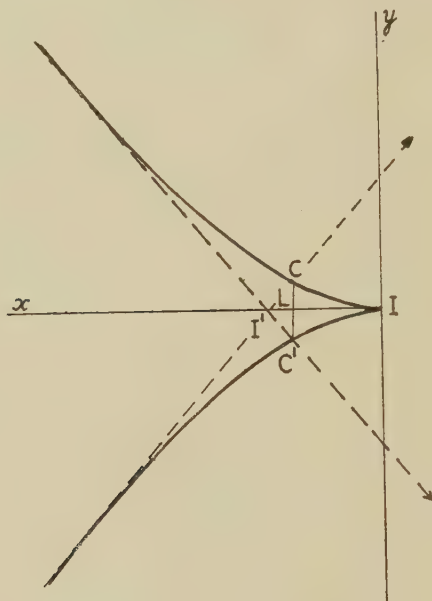
Figure 1.

plane $x = \frac{3}{4}At^2$ the radius is only $\frac{1}{4}At^3$. The best focusing position is thus not at the paraxial focus but at CLC', the *circle of least confusion*.

The optical computer usually plots longitudinal spherical aberration against the radius of the aperture stop and, assuming the higher orders of aberration to be negligible, the curve will be the parabola $y^2 = x/A$ (see figure 2).

In practice the higher orders are generally far from negligible, and the type of spherical aberration frequently obtained is shown in the same diagram, the curve being plotted from a trigonometrical trace of certain selected rays. The curve must necessarily have the same curvature on the axis as the first-order parabola, but for larger apertures it usually bends back from the parabola and even crosses the y-axis, giving over-correction at the edge. It is clear that, with spherical aberration of this kind, the caustic must be more complicated than the

FIRST − ORDER CURVE

PARABOLA

HIGHER − ORDER CURVE

ABERRATION

Figure 2.

OVER

CORRECTED − RAY

RAY

WITH

C

C′

ZERO ABERRATION

EXTREME

RAY THROUGH CLC″
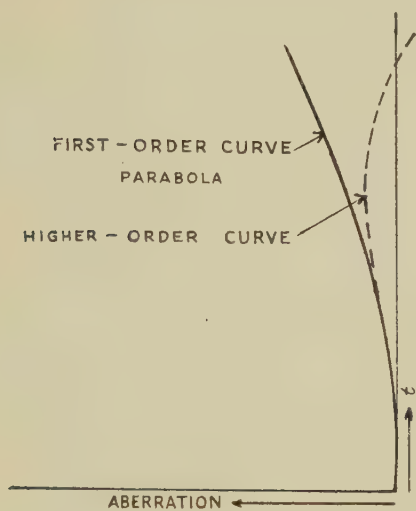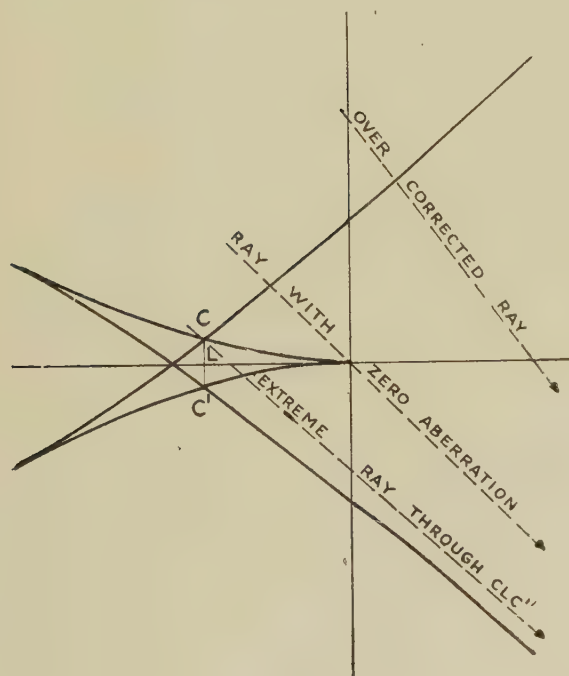
Figure 3.

semi-cubical parabola. The longitudinal spherical has reached a maximum at some point (generally known as the *zone*) about $0 \cdot 7$ to $0 \cdot 8$ times the full aperture, so that the caustic must necessarily possess two extra-axial cusps (see figure 3).

Let us, as the next stage of the investigation, assume that the longitudinal spherical can be adequately expressed as $At^2 - Bt^4$. This can only become zero when A and B are of the same sign, so that it is more convenient to write the expression as $At^2(1 - t^2/T^2)$, where T is the value of t for which the aberration becomes zero. The equation of the ray is now $y = xt - At^3(1 - t^2/T^2)$. The envelope is given by

$$x = 3At^2 - 5At^4/T^2, \qquad \ldots\ldots(1)$$

$$y = 2At^3 - 4At^5/T^2, \qquad \ldots\ldots(2)$$

where x and y are the co-ordinates of the point of contact of the ray with the caustic. Now equation (1) can be looked on as a quadratic in t^2 for the determination of the slopes of the caustic at the four points where it is cut by $x = x$. If this line passes through the extra-axial cusps, the quadratic in t^2 will have equal roots, giving $x = 0 \cdot 45 AT^2$. The slopes of the tangents at the cusps are $t = \pm T\sqrt{0 \cdot 3}$, so that the co-ordinates of the cusps are $0 \cdot 45 AT^2$, $\pm 0 \cdot 24 AT^3 \sqrt{0 \cdot 3}$.

There is a double point on the axis at $x = \frac{1}{4} AT^2$, and this is clearly the position for which the longitudinal spherical is a maximum. The slope of the caustic at this point is $\pm T/\sqrt{2}$.

There are two extra-axial double points whose co-ordinates are $0 \cdot 2 AT^2$, $\pm 0 \cdot 016 \sqrt{5} AT^3$, the slopes of the curve at these points being $t = \pm \frac{1}{10}(5 \pm \sqrt{5})T$.

The equation of the tangent line to the curve is

$$y = tx - At^3(1 - t^2/T^2),$$

so that through any arbitrary point (x, y) there are five tangents that can be drawn to the curve. If the point is the extra-axial double point $(0 \cdot 2 AT^2, 0 \cdot 016 \sqrt{5} AT^3)$, then each tangent line to the curve at this point will be counted twice in the quintic. Now at this point of the curve the slopes of the tangents are clearly

$$t = \tfrac{1}{10}(5 - \sqrt{5})T \quad \text{and} \quad t = -\tfrac{1}{10}(5 + \sqrt{5})T.$$

The equation for the determination of the five values of t becomes $t^5 - t^3T^2 + 0 \cdot 2tT^4 - 0 \cdot 016\sqrt{5}T^5 = 0$ and four of the five factors of the left-hand side are $\{t - 0 \cdot 1(5 - \sqrt{5})T\}^2 \{t + 0 \cdot 1(5 + \sqrt{5})T\}^2$. The fifth factor is $(t - 0 \cdot 4\sqrt{5}T)$, so that tangent lines which have slopes $t = \pm 0 \cdot 4\sqrt{5}T$ pass through the extra-axial double points. The longitudinal spherical for this ray is $0 \cdot 16 AT^2$, which is $0 \cdot 64$ times the maximum longitudinal spherical. Now it is clear from the shape of the curve (figure 3) that the smallest cross-section of the figure is that drawn through the extra-axial double points, and that the circle of least confusion cannot have a radius of less than $0 \cdot 016 \sqrt{5} AT^3$. All rays up to a slope $t = 0 \cdot 4\sqrt{5}T$ pass through this circle, but rays at steeper inclinations pass outside it.

It follows that if the first- and second-order terms are adequate to represent the longitudinal spherical, it does not pay to open the aperture beyond $0 \cdot 4\sqrt{5}T$,

or about 0.894 of the aperture for which the aberration is zero. An increase of aperture to T increases the circle of least confusion threefold. To go beyond that point and have over-correction at the edge makes matters much worse.

When we take in the next term in the longitudinal spherical we find additional reason for not reducing the aberration at the edge of the system beyond a certain degree of under-correction. This equation of the tangent can now be written

$$y = tx - At^3 + Bt^5 - Ct^7 \qquad \ldots\ldots(3)$$

and, once more, this equation can be regarded as one of the seventh degree to determine the directions of the seven tangents that can be drawn through the point (x, y) to touch the caustic. In the second-order caustic, the second-order term $-Bt^4$ just balances the first order At^2 when $t = T$. For higher values of t the second-order term will be the greater, the system will be over-corrected and the caustic will run away continuously to the right. The introduction of a third-order term makes it possible to stop the continuous drift of the aberration to the right. The third-order term must be of the same sign as the first order and of opposite sign to the second order, and there will then be a second zone where the aberration will again be stationary, either a minimum under-correction or a maximum over-correction. As a consequence the caustic will have two further cusps upon it, as it must finally, with this form of aberration, run away to the left. The ideal condition is that the curve, having crossed itself once at the lower double point C′ (figure 3), shall turn back and pass through the upper point C. In other words, we want a caustic with two triple points upon it. If (x, y) is one of the triple points, three of the seven solutions of equation (3) will each occur twice. This requires that the expression $t^7 - Bt^5/C + At^3/C - xt/C + y/C$ shall have a factor of the form $(t^3 - pt^2 + qt - r)^2$, the remaining factor being $(t + 2p)$, since the equation contains no term in t^6. This leads to the following relationships: $q = -2p^2$; $r = -p^3$; $p^2 = \frac{1}{2}A/B = B/7C = 2x/A$; $y/C = 2p^7$. From these we find $2B^2 = 7AC$, which is the condition that there shall be a triple point at all. When this condition is satisfied, the position of the point is $(\frac{1}{4}A^2/B, \pm A^{5/2}/14 . (2B^3)^{1/2})$.

We are now in a position to compare the second-order and third-order caustics.

	Second order	third order
Value of long. sph.	$At^2(1 - t^2/T^2)$	$At^2 - Bt^4 + 2B^2t^6/7A$
Radius of circle of least confusion (C.L.C.)	$0.03578AT^3$	$0.05051A^{5/2}/B^{3/2}$
x-coordinate of C.L.C.	$0.2AT^2$	$0.25A^2/B$
Slope of steepest ray passing through C.L.C.	$0.8944T$	$(2A/B)^{1/2}$

If, in the third-order caustic, we can obtain a value of B equal to $1.25A/T^2$, we get a circle of least confusion at $x = 0.2AT^2$ and of radius $0.03614AT^3$, which is practically identical with that of the second-order caustic. The slope of the steepest ray passing through the circle of least confusion is $1.2649T$. Thus the

available aperture has been increased in the third-order caustic by over 40 per cent without any sacrifice of definition.

The best form of caustic of the fourth order would have quadruple points at the top and bottom of the circle of least confusion and, by a choice of the ratio $B : A$, the size and position of this circle could be made substantially the same as before. With this caustic a still wider aperture would be available. In fact it is clear that the desirable curve of spherical aberration is not one that gives over-correction at the edge but one which is under-corrected everywhere by amounts which vary between maxima and minima. If it is impossible to achieve a curve of this type, and if, with increasing aperture, the curve necessarily runs away to over-correction, then nothing is gained by using the over-corrected parts of the lens. The light passing through them lies outside the circle of least confusion and fine detail is damaged, in photographic work, by swamping parts of the field near the centre by light which should not be there. It is a mistake for a designer to assume that he can have as much over-correction at the edge as he had of under-correction at the zone. If, for example we consider the case of a photographic lens of aperture f/2·9 designed on those lines, it will be just corrected at about f/3·2 and the zone will occur at about f/4·6. Rays up to about f/3·6 will all pass through the circle of least confusion and no increase can be made above that point without deterioration of the central definition. At the same time it must .be remembered that no stopping-down below f/3·6 will give any further improvement in definition until a much smaller aperture is reached. If a designer wants to produce a lens which is really f/2·9 and, in spite of all he can do in the way of altering his curves and refractive indices, the aberration curve persists in running away to the right after the zone, his best course is to aim at getting correction for about f/2·6, but not to use the lens beyond f/2·9. Of course, in making this statement it must be understood that the circle of least confusion must be kept within its desired limits. It is obviously no good correcting for f/2·6 if that can only be done at the expense of considerable increase in the spherical aberration at the zone.

It is worth while considering, in general terms, the most suitable rays to trace so that all the information possible may be obtained respecting the shape of the caustic near the circle of least confusion, which is the most important part in respect of the performance of the optical system. Different designers have different preferences, but a common plan seems to be to trace the edge ray and another at 0·7 of the semi-aperture. If the designer will stick to the limitation that the aberration should on no account change sign, and that the amount for the edge ray should not be less than two-thirds of that for the zone, then the circle of least confusion must necessarily be in the neighbourhood of the point where rays inclined at 0·8 and −0·3 cut one another. By tracing three rays, viz. the edge ray and the two just mentioned, valuable information will be obtainable respecting the definition and the manner in which it varies in and out of focus.

Finally, as a numerical example of a lens which has a triple point on the caustic,

and for which there are two zones, one of maximum and the other of minimum aberration, both under- or both over-corrected, let us suppose that the spherical aberration in millimetres can be expressed as $35t^2 - 1050t^4 + 9000t^6$. The triple point is at $(0\cdot292, \pm0\cdot0108)$. The circle of least confusion is thus about $3/10$ of a millimetre in front of the paraxial focus and only just over $1/50$ millimetre in diameter. All rays up to $f/1\cdot93$ pass through this circle. The caustic is drawn to scale in figure 4, except that the vertical scale is five times that of the horizontal in order to bring out the salient points.
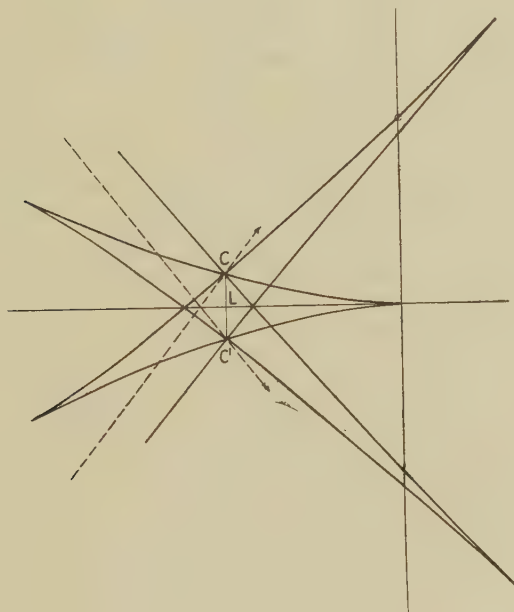
Figure 4.

This example is, of course, a freak. The rapidity with which A, B and C (35, 1050, 9000) are increasing suggests that it is most improbable that higher terms are negligible. The exact analysis of the shape of the caustic cannot therefore be insisted on. At the same time a lens system undoubtedly could be found which had a second zone in the spherical aberration. The caustic for the system *must* approximate in that case to that shown in figure 4.

EXPERIMENTS ON THE TEMPERATURE COEFFICIENT OF STATIC FRICTION

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ABSTRACT. Angles of repose of metals have been measured under controlled vacuum conditions.

Preliminary measurements were made at room temperature in air. As it was found that vibrations tended to reduce the angle of repose, they were eliminated. Naked metal surfaces were obtained for aluminium and cadmium by cleaning by volatilization in a high vacuum. Interesting results were found with a steel slider when a deposit of volatilized aluminium had formed on steel crutches.

Experiments on cadmium cleaned by volatilization at various temperatures at which the whole friction chamber was baked out were carried out in the range from $+176°$ c. to $-100°$ c. The results, in spite of the inevitable fluctuations of individual values at any particular temperature, clearly show a general drift with temperature, and are a first instalment towards an approach to the thermodynamical criterion for the fundamental mechanism of friction between *naked* metal surfaces. A conservative analysis of the results of measurements between $-100°$ c. and $+100°$ c. leads to a temperature coefficient of the angle of repose $d\bar{\alpha}/dt = -3\cdot5 \times 10^{-2}$ degrees, while a bolder interpolation would raise this numerical value by a factor of about two ($d\bar{\alpha}/dt = -8 \times 10^{-2}$ degrees). Above about $+100°$ c. the angle of repose of naked cadmium increased with rising temperature.

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§ 1. INTRODUCTION

IN the work described below, measurements have been made of the angle of repose of metals under controlled vacuum conditions. With cadmium, where cleaning by volatilization from the surfaces was possible, the measurements have been extended to cover a wide range of temperatures from $+176°$ c. to $-100°$ c., and a temperature coefficient of static friction * of very good reproducibility has been derived for the range of temperatures from $+100°$ c. to $-100°$ c.

§ 2. THE SIGNIFICANCE OF A TEMPERATURE COEFFICIENT OF SOLID FRICTION

Solid friction (between naked surfaces) must arise at the small irregularities of the surfaces in contact, which can suffer both *elastic deformation* and *abrasion*.

* It is of fundamental importance, as Dr. F. E. Simon, F.R.S., suggested some time ago, to determine whether such a temperature coefficient of friction between naked solids exists.

The existence of the temperature coefficient is a criterion for deformation as an essential part of the mechanism for the loss of energy by solid friction. In the case of deformation, the energy is dissipated to some extent by means of the heat conductivity of the materials; in the case of pure abrasion the only heat loss is the latent heat of vaporization. Over a wide range of temperatures, from the melting point of a solid down to the neighbourhood of the absolute zero, both the adiabatic compression energy and the thermal conductivity exhibit a marked dependence upon temperature. Therefore, the energy loss which is perceived as friction should exhibit a measurable temperature coefficient, if deformation of the surface irregularities is the elementary mechanism of solid friction. On the other hand, the latent heat of vaporization has only a very slight temperature coefficient below the melting point of a material, and if abrasion of molecules (even mon-atomic) from the irregularities of the surfaces in contact were the predominant action in solid friction, virtual independence of temperature could be expected. There is reason to believe that the force of friction between naked *metal* surfaces is a function of the temperature only, over a wide range of velocities of sliding, and therefore the variation of static friction with temperature should indicate directly the temperature coefficient of the energy loss by solid friction during a given displacement.

§3. EXPERIMENTAL

Method

A cylindrical metal rod resting on two pairs of V-shaped (90°) metal crutches (Shaw and Leavey, 1930) was free to travel to and fro between two buffers when the apparatus was tilted in either direction to the horizontal. Shaw and Leavey's apparatus, the great virtue of which was that an unlimited number of observations could be made without opening the friction chamber, had to be disconnected from the vacuum pump before the angle of repose could be measured, the atmosphere of residual gas being at a pressure certainly not less than 10^{-2} to 10^{-1} mm. Hg. The present apparatus was designed to remain connected with a high-vacuum pump (about 10^{-6} mm. Hg) throughout the operations of baking out and of making measurements. This involves turning the apparatus upside down * so as to separate the slider and crutches while baking out, and tilting it in either direction up to 90° to the horizontal to measure the angle of repose. Also it was to remain vacuum-tight, whilst its temperature was varied between $+450°$ c. and that of liquid air.

The friction mechanism is enclosed in a metal tube with one solid end and with a head (h, figure 1) bolted to a flange at the other end. The vacuum-tight joint is achieved by inserting two concentric washers of diamond-shaped cross-section, made of copper and invar respectively. At the higher temperatures the copper washer maintains the seal, and below room temperature the invar washer.

* The sliding rod rests on two Pyrex tubes instead of on the crutches during the baking-out process.

The sliding rod (5 cm. long) and the crutches were 3·17 mm. diameter, and the surfaces were finished on 0000-emery paper flooded with paraffin.

The movement of the rod is limited to 3·5 mm. by a rigid copper buffer (*b*, figure 1) at each end. When the rod makes contact with one of the buffers, *b*, it closes an electric circuit which ignites a neon lamp to indicate that sliding has taken place.
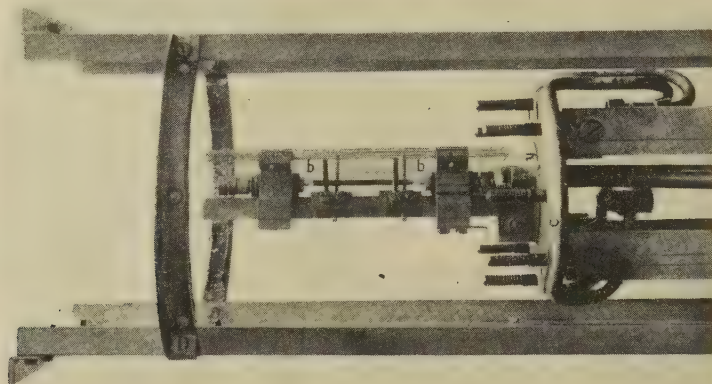
Figure 1. View of friction device.

The temperature of the friction elements is varied by heat conduction and radiation. The cylinder which encloses the friction chamber is double-walled with an open copper pipe of helical shape between the walls (figure 2), and a heating coil is wound on the outer copper cylinder. Temperatures below atmospheric are attained when a cooling agent is passed through the pipe C, which is brazed
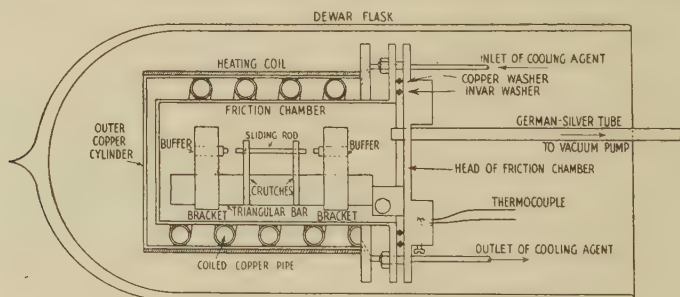
Figure 2. Apparatus.

on to the head *h*, and through the helical copper pipe (figure 2). This arrangement leads to a temperature gradient along the triangular bar supporting the crutches inside the friction chamber. The end of the bar secured to the head *h* assumes a slightly lower temperature than the opposite end. The electric heating coil produces a similar gradient at temperatures above atmospheric. When metal was volatilized in the friction chamber, the amount of condensed metal

was always largest on the inside of the head.   The measured temperatures were those of the head h, and were taken with a copper-constantan thermocouple. Since the primary object of the experiments was to show whether a temperature coefficient exists, it was sufficient to measure temperature changes at one end of the gradient.

Measurements at room temperature

Preliminary experiments were carried out in air with a rod and crutches made of a steel containing 1·2 to 1·5 % C, 0·35 % (max.) Mn.   External vibrations were apt to diminish the measured angles of repose, and their effect was practically eliminated by suitable alterations.   With a visible rust layer on the surface, no sliding took place, even at a tilting angle of 90° ($\mu = \infty$).   After the rust had been removed, and the friction chamber baked out at 450° C. at a pressure of about 10^{-6} mm. Hg with the slider out of contact with the crutches, an angle of repose α of 51° ($\mu = 0·9$; it follows from the geometry of the crutches supporting the rod that $\mu\sqrt{2} = \tan \alpha$) was measured, which gradually decreased and finally settled down between about 38° ($\mu = 0·5_5$) and 42° ($\mu = 0·6$).*

It is a matter of considerable experimental difficulty to remove the last traces of adsorbed matter and oxide films from a metal surface, and it is considered that *volatilization* from the metal surface in a high vacuum is the most reliable means of obtaining naked surfaces.   But even in this case, the surfaces can be preserved free from a continuous layer of contamination for a limited period of time only. Perfect cleaning was obtained with a sliding rod of aluminium † which was partly volatilized during the baking-out process.   When the temperature measured at the head, i.e. at the end of the gradient, where it had its lowest value, was 260° C., aluminium vapour condensed on the inside of the head and in its neighbourhood, while the rate of volatilization increased towards the far end of the aluminium rod, which, at about 10^{-6} mm. Hg, showed on the steel crutches angles of repose between 68°·5 ($\mu = 1·8$) and 54° ($\mu = 1$).   On opening the friction chamber, this rod was found to have acquired a coarse dendritic surface during volatilization, and to have slid on a deposit of aluminium on the steel crutches. This is an indication that even the far end of the crutches was at a temperature below the volatilization point of aluminium.   The sliding rod had been baked out while resting on the Pyrex tubes, and had been heated by radiation from the wall of the chamber.   Without cleaning the crutches, the aluminium rod was replaced by the steel rod previously used.   The chamber was evacuated again, and appreciably smaller angles of repose between 26° and 28° ($\mu = 0·35$) were found.   Repolishing the rod and crutches with 0000-emery until they acquired

* Fogg and Hunwicks (1940), with the Deeley machine modified by substituting three steel balls for the three flat pegs, measured coefficients of static friction between 0·56 and 0·60, when they resorted to the drastic method of removing the contaminated surfaces completely by abrasion with "0000 blue back" emery paper, and of performing their measurements immediately after such removal in order to keep re-contamination from atmospheric sources as small as possible.

† The aluminium was reasonably pure, containing 0·16 % Si, 0·28 % Fe and traces of Mg and Mn.

a bright appearance (the crutches with the aluminium deposit had a dull appear-
ance prior to repolishing), further *reduced* the angles to between $18°$ and $22°$
($\mu = 0.2$ to 0.3).   To prove that the reduction of the angle of repose was due to
the deposit itself as a mechanical aid, the friction chamber was baked out for many
days, and the gradual increase of the angle of repose was noted until angles between
$36°$ and $38°$ were reached again, when this experiment was discontinued.

The volatilization point of both friction elements was approached in the
case of a cadmium rod on cadmium crutches.   After such cleaning by volatiliza-
tion, the mean value of the angle of repose when measured at room temperature
was about $43°$ ($\mu = 0.6$ to 0.7).   Since individual measurements showed wide
fluctuations * even when the friction chamber with the cadmium specimens had
been baked out at $250°$ c., a large number of readings were taken at room tempera-
ture.   The mean values of the angles of repose obtained by tilting the friction
chamber in one direction were not always found to coincide with the mean values

Table 1

Baking-out temps. (°c.)	Observed min. and max. values of the angle of repose		Mean values				
	a_1	a_2	$\bar{a}_2$	No. of observations	$\bar{a}_2$	No. of observations	$\dfrac{\bar{a}_1 + \bar{a}_2}{2}$
160	36·5–52·5	38·5–47·0	41·7	16	42·8	15	42·2
	37·0–52·0	39·0–52·0	41·5	16	42·7	15	42·7
	42·5–53·5	34·5–57·0	45·4	11	41·9	12	43·6
	38·5–51·0	40·5–47·5	42·8	13	43·2	13	43·0
228	44·0–48·0	38·0–45·0	45·4	8	40·9	8	43·2

obtained by tilting the chamber in the opposite direction.   Table 1 contains
these mean values $\bar{a}_1$ and $\bar{a}_2$, and the width of the bands of fluctuations (extreme
values of α_1 and α_2).   All the measured angles lie between $34°.5$ and $57°.0$ and the
mean values between $42°.2$ and $43°.6$.   It is obvious from table 1 that the
individual values α_1 and α_2 are not distributed evenly between the extreme values.

As an example of a soft material of appreciably higher volatilization point,
a copper rod was used on copper crutches.   When the chamber was evacuated,
but not baked out, an angle of repose of about $43°.5$ ($\mu = 0.7$) was measured at
$21°$ c.   The friction chamber was then baked out, and the angle of repose was
measured, as it cooled down to room temperature.   After standing for three
days, a pressure of a few millimetres Hg had built up in the chamber.   Upon its
re-evacuation to 9.6×10^{-4} mm. Hg, an angle of repose of $62°.5$ ($\mu = 1.3_5$) was
measured at $20°$ c., which settled down to about $41°.4$ ($\mu = 0.6$) as the vacuum
further improved.

* It would appear plausible to suppose that minute evolutions of gas might cause such fluctuations
in the work with *naked* metal surfaces.

The results at room temperature are summarized in table 2.

Table 2

Sliding rod	Crutches	Remarks	Angle of repose	Coefficient of static friction
Steel	Steel	At atmospheric pressure with visible layer of rust on surfaces	>90°	∞
Steel	Steel	Baked out	51°	0·9
Steel	Steel	Final values, a few days after baking out	38°–42°	$0·5_5$–0·6
Copper	Copper	Before baking out	43°·5	0·7
Copper	Copper	At $9·6 \times 10^{-4}$ mm. Hg	62°·5	$1·3_5$
Copper	Copper	Pressure $\ll 9·6 \times 10^{-4}$ mm. Hg	41°·4	0·6
Aluminium	Deposit of aluminium on steel crutches	Baked out and volatilized	54°–68°·5	1–1·8
Steel	Ditto	—	26°–28°	$0·3_5$
Steel	Ditto	Rod and crutches repolished with 0000-emery	18°–22°	0·2–0·3
Steel	Ditto	Baked out for many days	36°–38°	
Cadmium	Cadmium	Baked out and volatilized	34°·5–57°	0·5–1·1

§ 4. THE TEMPERATURE COEFFICIENT

On general grounds, solid friction cannot assume a finite value in the close neighbourhood of the absolute zero of temperature, where entropy changes tend to vanish. At room temperature, solid friction assumes an appreciable finite value as the above-described experiments show. When the temperature of the surface of the lower-melting friction-element reaches the melting point, the force of friction between non-porous solids assumes a very small value because then the molten surface layers act as a lubricant, as indicated by the low values observed with ice at temperatures near its melting point (Jacob, 1912; Bowden and Hughes, 1939). From the absolute zero of temperature to the melting point the sign of the temperature coefficient of solid friction would thus change at least once, although no prediction could be made about either the existence or the sign of a temperature coefficient in the intermediate range of temperatures.

Cadmium, which can be cleaned easily by volatilization *in vacuo* at a temperature at which the whole friction chamber can be baked out, was chosen for measurements between $+176°$ c. and $-100°$ c. The results clearly show a trend with temperature in spite of considerable fluctuations * of individual values (figures 3 *a* and 3 *b*). The angle of repose of cadmium is found to increase with falling

* The crosses and circles in the diagrams indicate the mean values, whereas the range of individual values is represented by the vertical lines at the various temperatures. The positions of the crosses and circles on the vertical lines demonstrate that the individual values are not distributed evenly between the extreme values at any given temperature.
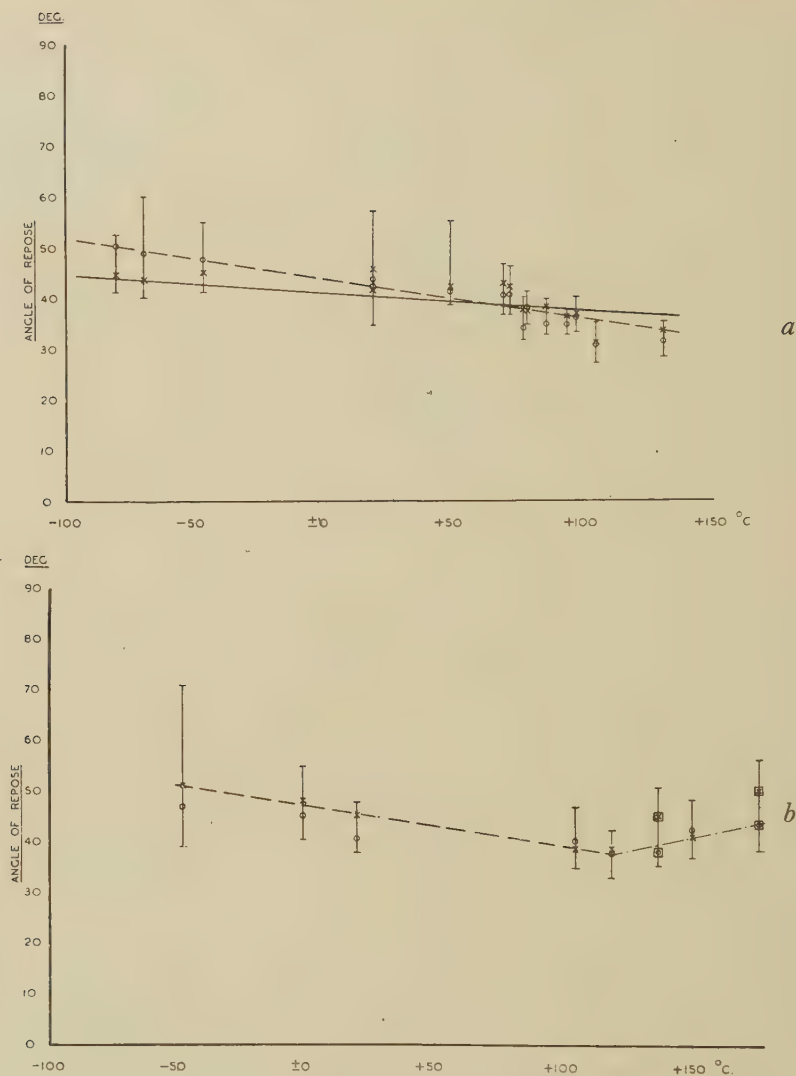
Figure 3. Angles of repose of cadmium on cadmium at various temperatures. The crosses and circles indicate the mean values of the critical angles obtained by tilting the friction chamber in opposite directions, whereas the range of individual values is represented by the vertical lines.

a. After friction chamber had been baked out at $+160°$ c.

b. After friction chamber had been baked out at $+228°$ c. The results at $+137°$ c. and $+176°$ c. were obtained in a separate series of experiments when the chamber had been baked out at $+250°$.

temperature in the range from $+100°$ c. to $-100°$ c. (table 3). Figure 3 *a* was obtained after the friction chamber had been baked out at $160°$ c. The plotted curves are arbitrary interpolations which indicate that even a conservative analysis of the results (full line, figure 3 *a*) shows a general drift in the direction suggested.

The dotted line was inserted with the intention of demonstrationg that a bolder interpolation would raise the numerical value of the temperature coefficient by a factor of about two. The reproducibility of the results was checked by measuring some further points * in the neighbourhood of temperatures at which measurements had been taken previously. The values found at 94° C. ($\bar{a}_1 = 36°{\cdot}3$; $\bar{a}_2 = 34{\cdot}4°$) agree satisfactorily with those found previously at 97°·3 C. ($\bar{a}_1 = 36°{\cdot}6$; $\bar{a}_2 = 35°{\cdot}8$), those at 78°·5 C. ($\bar{a}_1 = 37°{\cdot}4$; $\bar{a}_2 = 37°{\cdot}8$) with those at 77° C. ($\bar{a}_1 = 37°{\cdot}6$; $\bar{a}_2 = 33°{\cdot}8$), those at 69°·5 C. ($\bar{a}_1 = 42°{\cdot}7$; $\bar{a}_2 = 40°{\cdot}3$) with those at 72° C. ($\bar{a}_1 = 42°{\cdot}0$; $\bar{a}_2 = 40°{\cdot}2$), and those at 19° C. ($\bar{a}_1 = 45°{\cdot}4$; $\bar{a}_2 = 41°{\cdot}9$) with the other values obtained at room temperature (see table 1).

Table 3

Baking-out temperatures (°C.)	Mean values of the angle of repose	Temperature coefficients		Remarks
		$\dfrac{d\bar{a}}{dt}$	$\dfrac{d\mu}{dt}$	
160	$\bar{a}_{-100° \text{ C.}} = 44°{\cdot}5$ $\bar{a}_{+100° \text{C.}} = 37°{\cdot}5$	$-3{\cdot}5 \times 10^{-2}$	$-7{\cdot}5 \times 10^{-4}$	Full line of figure 3 a
	$\bar{a}_{-100° \text{ C.}} = 52°$ $\bar{a}_{+100° \text{ C.}} = 36°$	-8×10^{-2}	$-19{\cdot}5 \times 10^{-4}$	Dotted line of figure 3 a
228	$\bar{a}_{-50° \text{ C.}} = 51°{\cdot}25$ $\bar{a}_{+100° \text{C.}} = 39°{\cdot}25$	-8×10^{-2}	$-20{\cdot}2 \times 10^{-4}$	Dotted line of figure 3 b

In spite of the fluctuations of individual values it seems reasonable to derive from these results a conservative *lower* limit for the temperature coefficient of cadmium by extrapolating along the full line of figure 3 a from $-100°$ C. to $+100°$ C., with the result that $d\bar{a}/dt = -(3{\cdot}5 \times 10^{-2})$ degrees per $+1°$ C. and $d\mu/dt = -7{\cdot}5 \times 10^{-4}$ per 1° C. (table 3). If the extrapolation were taken along the dotted line, a higher temperature coefficient $d\bar{a}/dt = -(8 \times 10^{-2})$ degrees per $+1°$ C., would be derived. From figure 3 b, which summarizes independent results obtained when the friction chamber had been baked out at 228° C., a temperature coefficient $d\bar{a}/dt = -(8 \times 10^{-2})$ degrees per $+1°$ C. would follow as the result of an interpolation in the range from $-50°$ C. to $+100°$ C. This is in good agreement with the result deduced from figure 3 a. It appears that above $+100°$ C. the angle of repose increases again, as the result obtained at $+150°$ C. suggests. Observations made at $+137°$ C. and $+176°$ C. in a *separate* series of experiments when the friction chamber had been baked out at 250° C. fit very well with the results obtained at $+150°$ C. and support the view that the curve of figure 3 b rises between about $+100°$ C. and $+200°$ C. The following values were found at $+137°$ C.: $\bar{a}_1 = 45°{\cdot}3$; $\bar{a}_2 = 38°{\cdot}2$ (with a range of fluctuations of $\bar{a}_1$ between 40°·5 and 51°·0 and of a_2 between 35°·5 and 49°·0), and at $+176°$ C.:

* These points are also shown in figure 3 a.

$\bar{a}_1 = 50°{\cdot}2$, $\bar{a}_2 = 43°{\cdot}7$ (with a range of fluctuations of a_1 between $44°{\cdot}0$ and $56°{\cdot}5$ and of a_2 between $38°{\cdot}5$ and $55°{\cdot}5$).

It is apparent from some preliminary measurements with a sliding rod of copper on copper crutches that, in this case of a soft metal " cleaned " *in vacuo* at a temperature below its volatilization point, the dependence of friction upon temperature is much less conspicuous than that of cadmium. The angles measured at room temperature almost coincide with those measured for cadmium. Up to about $100°$ c. the values for copper remain nearly independent of temperature. As the temperature is still further increased, they show a tendency to rise.

§ 5. DISCUSSION

In the experiments described above, the coefficients of static friction of metals, which while out of contact were baked out in a high vacuum, were found to be somewhere between, say, $0{\cdot}5$ and $1{\cdot}8$. These results were obtained with steel on steel, with aluminium on steel carrying a deposit of volatilized aluminium, with copper on copper, and with cadmium on cadmium. The existence of a negative temperature coefficient was established with friction elements of cadmium in the range from $-100°$ c. to $+100°$ c. Above $+100°$ c. the sign of the temperature coefficient appears to change. The trend of the angle of repose with temperature is apparent even when the wide bands of fluctuating values are plotted at the various temperatures. It might be thought that measurements with very soft materials like cadmium, in which deformation in the neighbourhood of points of contact is certain to occur on account of the inevitable stress concentration there, would yield little information as to the nature of friction, since the plastic properties of cadmium depend on temperature. However, no noticeable temperature coefficient of friction could be expected, even though the plastic properties of cadmium do depend on temperature, if abrasion alone were responsible for the elementary mechanism of friction. The fact that these properties and the coefficient of friction both depend on temperature, is an argument in favour of the essential part played by deformation in the mechanism of solid friction. The reason why cadmium was chosen for these experiments is that cadmium can be cleaned by volatilization *in vacuo* at a temperature at which the whole friction chamber can be baked out.

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CONTACT ELECTRIFICATION OF SOLID PARTICLES

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ABSTRACT. Solid particles carry with them electrostatic charges from contact with the storage vessel. The sign of the charge acquired in the air of the laboratory was determined for metal particles which were poured either from a silica bowl or from a glass beaker, and for particles of insulators and semiconductors which parted contact with containers of silica, glass or various metals. A closed, insulated, metal funnel which is connected to an electroscope receives the charge which the particles carry with them from contact with a container from which they are poured. When the particles are made to stream from the funnel after the electrostatic charge has been removed from it, the funnel again acquires a certain charge, while the particles carry the opposite charge with them to the receptacle. Copper filings poured from a container of either glass or silica assume a positive charge, and silica particles poured from a copper trough assume a negative charge, while silica in bulk assumes a positive charge when it is rubbed against copper in bulk. Antimony powder poured from a container of either glass or silica assumes a negative charge, and both glass and silica in bulk rubbed against a block of antimony assume a positive charge.

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§1. INTRODUCTION

IN a previous communication (Schnurmann, 1940) emphasis had been laid on the point that cases of electrification by either friction or impact should be regarded as cases of *contact* electrification, and two experiments in particular were described to illustrate the separation of electrostatic charges when two different materials parted contact. In one of these (Coehn and Lotz, 1920) a paraffin-coated hollow metal sphere was removed from a beaker of distilled water in which it had been immersed. In agreement with Coehn's first rule, the paraffin was found to carry with it a *negative* charge, while the water retained the corresponding *positive* charge. In the other experiment silica flour was poured from a brass tube which was held insulated in a block of paraffin wax, so that both the negative charge carried away by the silica particles and the positive charge retained by the emptied brass tube could be observed. While it is easy to picture the contact electrification between two bare metal surfaces in a high vacuum as being the consequence of an exchange of electrons corresponding to the difference in the work functions of the two metals, the mechanism of

contact electrification is still puzzling in all other cases which are not associated with a chemical reaction. Certain empirical rules have been derived, such as Coehn's first and second rule for dielectrics and the rule that the contact electrification between a bare metal and a dielectric in a high vacuum can be predicted from the electrochemical properties of the metal and the ability of the dielectric to accept both electrons and positive ions.

Since electric charges are mobile at the surface of a metal, the charge separation between two metals in direct contact is independent of the area of contact. On the surface of a dielectric material, on the other hand, the positions of the static charges are fixed, and, therefore, the charge separation between either a metal and a dielectric, or between two dielectrics, must depend upon the actual area of contact. The proportionality between the charge separation and the area of contact at various contact pressures between a hard spherical dielectric and a softer plane one was shown by Hess (1932) with experiments done *in vacuo* at a pressure of a few times 10^{-3} mm. Hg.

§ 2. METAL PARTICLES

In air at atmospheric pressure, the magnitude of the observed electrification per unit area of contact is smaller than *in vacuo*, and it is rather astonishing to find that with many materials a very small volume of particles suffices to produce a large divergence of the leaves of an electroscope when the particles are poured from a glass beaker, for instance, on to an insulated metal disk which is connected to the electroscope. It is remarkable too that the inevitable contamination of the surfaces in the air of the laboratory does not seem to affect the qualitative results. Coehn and Curs (1924) had observed the sign of the charge acquired by metals which had been baked out in a high vacuum and made to slide along the baked-out walls of different dielectric materials in the same vacuum (table 1).

Table 1. Sign of electrical charge on metals (degassed)

	Quartz	" Felsenglas "	Glass
Zinc	—	—	—
Cadmium	+	—	—
Tin	+	—	—
Lead	+	+	—
Copper	+	+	+
Mercury	+	+	+
Silver	+	+	+
Platinum	+	+	+

While such careful procedure is required to ascertain that the results do not depend upon the presence of layers of adsorbed and condensed matter, it is interesting

to note that metal particles poured from either a bowl of vitreous silica or from a glass beaker in the air of the laboratory assume similar charges (table 2).

Table 2. Sign of electrical charges on metals (natural state)

	Vitreous silica	Glass
Antimony powder	—	—
Zinc granules (Analar)	—	—
Tin granules (Analar)	+	—
Lead shot	+	—
Brass turnings	+	+
Copper filings	+	+

§3. PARTICLES OF INSULATORS AND SEMICONDUCTORS

Many insulators and semiconductors, either powdered or crushed, assume a negative charge when poured either from a glass beaker or from a bowl of vitreous silica (table 3).

Table 3. Sign of electrical charge on dielectrics

	Vitreous silica	Glass
Copper oxide powder		—
Ferric oxide ,,		—
Chromic oxide ,,	—	—
Emery ,,	—	—
" Diamantine " ,,	—	—
Carborundum ,, 2F	—	—
Tungsten carbide powder		—
River sand	—	—
Crushed cooking salt	+	—
Small sodium thiosulphate crystals	—	—
Crushed sodium acetate (recryst.)		—
,, Rochelle salt (Analar)	—	—
,, potassium chloride (recryst.)	—	+
,, potassium bromide		—
,, potassium chlorate	—	—
,, ammonium chloride	—	—
,, ammonium oxalate $((NH_4)_2C_2O_4 . H_2O)$	—	—
,, barium chloride	—	—
Small copper sulphate crystals $(CuSO_4 . 5H_2O)$		—
Copper carbonate powder $(Cu_2CO_3(OH)_2)$	—	—
Magnesium carbonate powder	+	—
Small nickel sulphate crystals $(NiSO_4 . 7H_2O)$	—	—
Crushed lead chloride	—	—
Crushed boric acid	—	—
Borax powder	—	—
Calcined china clay powder	—	—

Sir Ambrose Fleming (1941) obtained the most uniform results when the powder of silica or sulphur was poured from a glass or metal container into a small tin funnel held above the receptacle on the electroscope. The application of a metal funnel between the container from which the particles are poured and the receptacle provides a very striking demonstration of the making and breaking of *contact* of a solid particle with the surface of a solid as the essential action for the electrostatic charge separation; it also shows that the velocity with which a particle strikes a metal surface is immaterial.

A funnel of monel metal with a long stem (length 25 cm., internal diameter 0·7 cm.) was held insulated in a block of paraffin wax. The bottom end of the funnel was closed with a rubber stopper, and the funnel was connected to an electroscope. River sand was poured from a glass beaker into the funnel; the leaves of the electroscope diverged with a *negative* charge. After the pouring operation the funnel was connected to earth for a minute, so that the static charges were conducted away. Subsequently the rubber stopper was removed from the funnel. While the sand streamed from the funnel into the receptacle, the leaves of the electroscope (which was still connected to the funnel) diverged again, this time with a *positive* charge. The sand particles carried with them a negative charge from the contact with the funnel, as was observed when the receptacle was connected to the electroscope. To make quite sure that the final charge acquired by the particles had been acquired during contact with the walls of the funnel, similar experiments were made with materials which carried with them a negative charge from the contact with glass, and a positive charge from contact with monel. Either crushed cooking salt, calcined china clay powder, crushed potassium chlorate, magnesium carbonate powder or borax powder was poured from a glass beaker into the monel funnel, which was closed at the bottom end and was connected to the electroscope, the leaves of which diverged in each case with a negative charge. After connecting the filled funnel to earth for a moment, the rubber stopper was removed. The leaves of the electroscope diverged again with a negative charge, as the particles of either of the above materials streamed from the funnel into the receptacle, which now assumed a positive charge. When the receptacle was connected to the electroscope, and crushed cooking salt was poured from a glass beaker into the monel funnel, so that a steady slender stream of particles fell into the receptacle, the leaves of the electroscope were at first observed to diverge, then to converge, and finally to diverge with a *positive* charge.

In most of the experiments with the monel funnel, the axis of symmetry of the funnel was at an angle to the vertical. When Rochelle salt was poured from a glass beaker into the insulated funnel, so that a steady stream of particles fell into the receptacle, the funnel assumed a strong negative charge, whereas the receptacle did not receive any charge; at any rate the leaves of the electroscope did not diverge when it was connected to the receptacle. When again the bottom end of the funnel was closed, and the funnel was connected to the electroscope, pouring of Rochelle salt from a glass beaker into the funnel made the

leaves of the electroscope diverge strongly with a *negative* charge. The funnel was then connected to earth for a minute, and after that the rubber stopper was removed from the funnel. The leaves of the electroscope did not now diverge

Table 4. Sign of electrical charge on materials from metal container

Material	Copper trough	Tin	Insulated monel funnel	Insulated brass tube
Emery powder	—		—	
" Diamantine " powder	—	—		
River sand	—	—	—	—
Crushed boric acid	—	—	—	—
,, potassium chloride (recryst.)	—		—	
,, ammonium chloride	—			
,, barium chloride			—	
,, lead chloride			—	
,, ammonium oxalate	—			
Copper carbonate powder	—			
Small nickel sulphate crystals	—			
Crushed Rochelle salt (Analar)	0		0	
,, potassium chlorate	—	—	+	
Calcinated china clay powder	—	—	+	
Borax powder			+	
Carborundum powder 2F	+			
Magnesium carbonate powder	+		+	
Crushed cooking salt	+	+	+	

when the Rochelle salt streamed from the funnel into the receptacle. Table 4 summarizes the sign of the charge which particles of various materials carry with them when they are either poured from a metal container or made to stream from an insulated monel funnel.

§4. DISCUSSION

The fundamental fact to be noticed is that electrostatic charges of opposite sign are separated whenever two different materials part contact. No particular group of materials was found to which this would not apply. The powders ought not to be damp; on wet days they were slightly heated ($30°$ c. to $40°$ c.) immediately before each experiment. The sign of the separated charges was well reproducible throughout. The working with solid particles involves the difficulty that they carry charges with them from contact with the walls of the storage vessel. It may thus happen that, for instance, crushed cooking salt which acquires a positive charge in contact with vitreous silica and a negative charge in contact with glass does not convey a charge to the receptacle when it is poured first from a silica bowl into a glass beaker and thence into the receptacle, which is

connected to the electroscope. If the particles are made to pass through either a funnel or a diaphragm on the journey from the container to the receptacle, both the sign and magnitude of the charge which the receptacle acquires depend upon whether the particles carry charges of the same sign with them from the contact with the container and from contact with either the funnel or the diaphragm. An insulated metal funnel which is used alternatively as a receptacle for particles and as a container from which particles are made to stream is a useful aid for deciding on the sign of the contact electrification.

The observation had been made previously by Sir Ambrose Fleming and by the author that silica in bulk assumed a *positive* charge when it was rubbed against copper in bulk, whereas at room temperature silica flour poured from a copper trough carried with it a *negative* charge, and copper filings poured from a bowl of silica carried with them a *positive* charge. In the first case the heat of friction raises the temperature of the surface irregularities of the silica and facilitates the migration of positive ions from the copper to the silica. If this is generally the case, the charge assumed by a base metal in frictional contact with silica must always be negative and independent of whether the metal is used as a powder or in bulk. Antimony powder at room temperature was observed to assume a negative charge when it was poured either from a bowl of vitreous silica or from a glass beaker. Similarly, both silica and glass in bulk rubbed against a block of antimony were observed to assume a positive charge. It appears that both negative and positive carriers contribute to the contact electrification between a metal and an insulator, and Sir Ambrose Fleming's conclusion that " when particles of a good insulator . . . . strike with some velocity a metal surface or one in which there are many free electrons, electrons tend to pass from the medium in which the electron density is large to the one in which it is small " must be modified before it can be of general application. There is evidence that the sign of the separated charges depends upon the work function and the solution pressure of the metal with respect to the dielectric, base metals assuming a negative charge in contact, for instance, with glass, and noble metals assuming a positive charge. Metal particles with oxidized surfaces exhibit charges of opposite sign. Pulverized zinc, for instance, poured from a glass beaker assumed a positive charge, and oxidized copper filings poured from a glass beaker assumed a negative charge. I have verified Sir Ambrose Fleming's (1939) result that an insulated perforated zinc sheet through which river sand passes when poured from a glass beaker assumes a positive charge, the sand conveying a negative charge to the receptacle. In similar experiments with crushed cooking salt and with calcined china clay powder, the zinc diaphragm assumed a negative charge and the receptacle a positive charge. All three materials assume a negative charge when poured from a glass beaker, but while silica particles assume a negative charge in contact with an oxidized zinc surface (pulverized zinc poured from a glass beaker carries a positive charge with it, whereas bright zinc granules carry a negative charge with them), particles of cooking salt and of calcined china

clay appear to assume a positive charge in contact with an oxidized zinc surface. The correctness of this explanation can be checked by making use of the results summarized in table 4. These show that crushed cooking salt carries a positive charge with it, while calcined china clay powder carries a negative charge with it when either of these materials is poured from a copper trough instead of a glass beaker. When the particles are poured so that they pass the perforated zinc sheet, one must expect the cooking salt to convey a positive charge to the receptacle, and the calcined china clay to carry no more than a small negative charge to the receptacle. This was observed to be the case, and it was found that in both cases the leaves of the electroscope diverged with a negative charge when the electroscope was connected to the zinc sheet.

Whatever the mechanism of the universal phenomenon of contact electrification may be, the work required for generating electric energy by this method is done by means of the mechanical separation of the surfaces which carry charges of opposite sign. It is certain, therefore, that the force of sliding friction must have an electrostatic component in all those cases in which the position of the charges on the surfaces is fixed, because, to maintain relative sliding, work must be done against the electrostatic attraction between the electrostatic charges of opposite sign. Haykin and his associates (1933 and 1940) were the first to demonstrate that relaxation oscillations can be generated with a frictional contact. It is hoped to show in a following paper that slow sliding proceeds by a process of apparent stick and slip when it is accompanied by the building up of an electrostatic contact potential.

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THE MEASUREMENT OF CONTACT ANGLES

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Lecture delivered 3 *January* 1941.   *MS. received* 19 *June* 1941

T HE determination of contact angles is a matter of some importance and of no small difficulty.   In dealing with flotation problems or, generally, with problems of wetting and detergency, certain coefficients are commonly employed which are measured in terms of the surface tension or free surface energy (γ) and the contact angle (θ) between a liquid and some specified solid. The practical importance of a knowledge of these capillary constants, and specially that of the contact angle, will be realized when we remember that the mass of ore treated by flotation processes is measured in millions of tons yearly.

It is worth while to note that experiments to determine these constants may be made with relatively simple apparatus and methods, and that workers who have but limited resources at their disposal may make very useful contributions to the advancement of knowledge in this direction.   One word of warning may be given here—it is impossible to be too careful in ensuring cleanliness of the surfaces concerned, and methods employed in cleansing apparatus should always be stated in detail.   The contact angles given by some experimenters are to be considered rather as illustrating the state of contamination of the surfaces employed than as measuring the contact angle between the liquid and a clean surface. It may, of course, be important, on occasion, to investigate any possible relation between the contact angle and the degree of contamination of the surface considered.

Two coefficients may be mentioned which continually appear in the literature of the subject, and are determined in terms of γ and θ—the work of adhesion (W) between a solid and a liquid, and the spreading coefficient (Σ).

The work of adhesion is the work expended in separating unit area of a liquid (L) from a solid (S) and is given by

$$W_{SL} = \gamma_{SA} + \gamma_{LA} - \gamma_{SL}, \qquad \qquad \ldots\ldots(1)$$

as is immediately obvious when we remember that γ stands for free surface-energy per unit area, and that in the separation involved, a solid-air and an air-liquid surface are formed and a solid-liquid surface disappears.   Moreover, consideration of the change in potential energy ensuing on a small displacement

of a system consisting of liquid in contact with air and with a solid gives at once

$$\gamma_{SA} = \gamma_{SL} + \gamma_{LA} \cos \theta, \qquad \dots\dots(2)$$

so that

$$W_{SL} = \gamma_{LA}(1 + \cos \theta), \qquad \dots\dots(3)$$

giving W in terms of the surface tension and the contact angle.

The value of the spreading coefficient Σ (Harkins and Feldman, 1922) determines whether or not a liquid shall spread over the surface of a solid; or a liquid A over the surface of a second liquid B.   For spreading to occur, the spreading coefficient must be positive, and, when considering the case of two liquids, the conditions for the spreading of A on B must be carefully distinguished from those holding when B spreads on A.   If W_1 is the work of adhesion for the interfacial surface, W_2 the work of cohesion " *of the liquid which is applied to the surface of the other liquid or the solid upon which the spreading might occur* ", then Σ is defined by the equation

$$\Sigma = W_1 - W_2 = \gamma_A - (\gamma_B + \gamma_{AB}), \qquad \dots\dots(4)$$

inasmuch as

$$W_1 = \gamma_A + \gamma_B - \gamma_{AB}, \quad W_2 = 2\gamma_B,$$

by the principles involved in the formation of equation (1).

Thus a liquid will not spread over the surface of another liquid (or solid) if its work of cohesion is greater than the work of adhesion.   Evidently Σ may be determined in terms of measurable surface tension and contact angles.

Restricting ourselves to the case of a liquid spreading over a solid, and reverting to our previous notation, we have

$$\Sigma = \gamma_{SA} - \gamma_{SL} - \gamma_{LA} \qquad \dots\dots(4\ a)$$

or, in terms of W,

$$\Sigma = W - 2\gamma_{LA} = \gamma_{LA} (\cos \theta - 1). \qquad \dots\dots(4\ b)$$

This article summarizes a number of the various methods that have been used to measure contact angles.   It must again be emphasized that the value of the contact angle is influenced most markedly by the cleanliness, or lack of cleanliness, of the solid surface concerned, and it is clear that a number of finite angles of contact quoted in the literature tend to vanish with increasing cleanliness of the solid surface in question.   Thus, in the article dealing with contact angles in the *International Critical Tables* (1928) it is noted that various methods point to a zero value for the contact angle between glass and water, alcohol, benzene, carbon tetrachloride, chloroform, acetic acid, glycerol, ether, turpentine, olive oil and hydrogen peroxide.   The authors of the article further remark that for a hundred other liquids a zero contact angle with glass is indicated by the agreement between the values of surface tension obtained from drop-weight and bubble-pressure experiments and those obtained from capillary-rise experiments in which the contact angle is assumed to be zero.

In the classic case of water in contact with glass, Volkmann (1894) " has found a^2 for water = constant $\pm 0 \cdot 0002$ at $20° \cdot 2$ c. for seven different kinds of glass, and Carver and Hovorka (1925) found a^2 for water = constant $\pm 0 \cdot 0002$ at $20°$ c. for glass, zinc, copper and silver ". Reference to this last-mentioned paper shows, however, that the authors have unwittingly employed a method for the determination of a^2 which is independent of the contact angle, so that their results can hardly be appealed to as showing a zero (or constant) contact angle for water in contact with the solids employed.*

The distinction between the values of the contact angle for advancing and for retreating menisci is most important, and must be kept clearly in view. Adam and Jessop (1925) have invoked what has been termed a force of friction (X) to obtain a relation between the advancing, retreating and equilibrium values of the contact angle. If such a *generalized* force (its dimensions are obviously MT^{-2}, those of surface tension) be supposed to act, equation (2) becomes, for an advancing contact angle (θ_1),

$$\gamma_{SA} = \gamma_{SL} + \gamma_{LA} \cos \theta_1 + X$$

and for a receding contact angle (θ_2)

$$\gamma_{SA} = \gamma_{SL} + \gamma_{LA} \cos \theta_2 - X.$$

Combined with (2) this gives

$$2 \cos \theta = \cos \theta_1 + \cos \theta_2.$$

It may be noted that it is the receding contact angle which is important in flotation problems (Adam, 1938).

It is not easy to classify completely the various methods that have from time to time been used to determine contact angles. A rough grouping may be made into (1) those methods which depend on more or less simultaneous determinations of γ and of $\gamma \cos \theta$, (2) methods which involve a determination of $\cos \theta$ without necessarily determining γ, (3) those methods which determine θ directly. It must be remembered that methods which result in a determination of $\cos \theta$ demand a high order of experimental accuracy where small contact angles are involved, inasmuch as the variation of $\cos \theta$ is very slow for small values of θ (the cosine of $8°$, for example, is $0 \cdot 990$).

Of methods in the first group, by far the best known is that in which the values of γ and $\cos \theta$ are deduced from measurements made on " large " bubbles or sessile drops, and the modern study of this method dates from a well known paper by Worthington (1885), who corrects the results of some earlier measurements of large bubbles and drops made by Quincke (1871). Interest in Worthington's paper has recently been revived (Burdon, 1940) and it may be desirable to note certain points raised in modern discussions of Worthington's paper, as

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* a^2 is identical with $\gamma/g\rho$ according to the practice of some writers, with $2\gamma/g\rho$ according to others. The dimensions of a are those of length. For water at ordinary temperatures $\gamma/g\rho$ has the value $0 \cdot 075$ sq. cm. Hence if $a^2 = \gamma/g\rho$, the value of a for water is about $2 \cdot 7$ mm.

values both of contact angles and surface tension are still deduced from measurements made on large bubbles and drops and formulae are used in circumstances in which their validity is very much open to question. Attempts have been made to saddle the mathematicians with the responsibility, as when Burdon (1940, p. 6) remarks that "it is often safest to regard the value obtained for the surface tension merely as a measure of the success of the mathematical analysis". This is hardly fair to the analysts who, since the days of Laplace and Poisson, have been perfectly clear and correct concerning the circumstances in which their formulae are valid, and, indeed, Worthington's paper is devoted to criticism of Quincke on the ground that he had neglected the warnings of the mathematicians, and had employed over-simple formulae which neglect the effect of the finite radius of the bubble and the radius of curvature at its vertex.

Worthington uses equations which are, if we allow for mere differences of notation, virtually those established by Poisson (1831). The main purpose of Worthington's paper is to amend Quincke's experimental results, and he is not concerned with the development of new formulae. Some writers who have recently discussed Worthington's paper have quoted Poisson's equation in a form which is, as far as I am aware, nowhere used by Worthington, and is, moreover, a form which tends to conceal the true nature of the approximations involved. The determination of a contact angle by this method involves a knowledge of the values of h, k and r, where these symbols have the significance shown in the figure, which represents an air-bubble, large enough to be sensibly plane at the
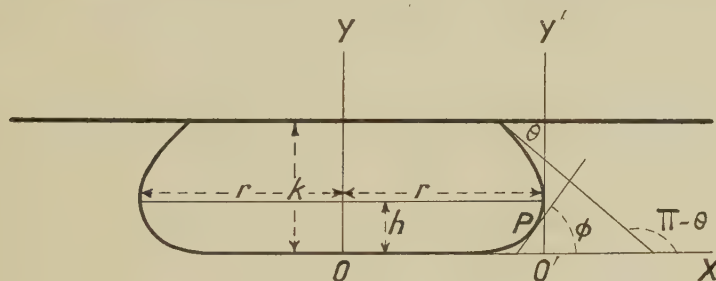
Figure 1.

vertex O, imprisoned under a plane sheet of, say, glass. Many analysts, among whom Poisson takes a high place, have developed equations which give the capillary constants γ and θ in terms of h, k and r. In discussing Worthington's paper, Burdon (loc. cit.) remarks, *à propos* of the effect of curvature in horizontal planes through the bubble, that *Worthington's* " evaluation of the total effect of this curvature leads to a formula (for $r > 2$ cm.) which may be written

$$\gamma = \tfrac{1}{2} g \rho h^2 \frac{1 \cdot 641 r}{1 \cdot 641 r + h} \text{ ",}$$

If we use the notation $a^2 \equiv \gamma/g\rho$, this becomes

$$2a^2 = h^2 \frac{1 \cdot 641 r}{1 \cdot 641 r + h}. \qquad \ldots\ldots(5)$$

The formula used by Worthington to correct Quincke's results is simply the Laplace-Poisson equation. He uses the notation K for the total depth of the bubble, $(K-k)$ for the quantity we have denoted by h, b for the radius of curvature at the vertex O, T for surface tension, D for density, and arrives at the equation

$$T = \frac{(K-k)^2}{2} \cdot D + \frac{2T}{b}(K-k) - T\int_0^{K-k} \frac{\sin\phi}{x}\,dz.$$

He quotes Laplace and Mathieu for the value of the integral and for $1/b$, and so deduces

$$\frac{T}{D} = \frac{(K-k)^2}{2} + \frac{T}{D} \cdot 2(K-k)\left(\frac{1}{b} - \frac{1}{3\cdot282L}\right). \qquad \ldots\ldots(6)$$

If in this equation we regard $1/b$ as negligibly small—that is, assume the bubble to be plane at the vertex—put a^2 for T/D, h for $K-k$, and r for L, we obtain

$$2a^2 = h^2 - \frac{4a^2h}{3\cdot282r} = h^2\left(1 - \frac{h}{1\cdot641r}\right), \qquad \ldots\ldots(7)$$

if we put $2a^2 = h^2$ in the small term. The equations (5) and (7) are strictly equivalent if we assume that terms in h^2/r^2 are negligible in comparison with unity, and the classic Poisson formula is preferable as it brings out this point clearly. It is, in fact, *not* the radius of the bubble which is the factor determining the validity of the formula but the magnitude in comparison with unity of the dimensionless quantity h/r, or, what comes to the same thing, a/r, since, very approximately, $2a^2 = h^2$.

It is very important to have clear views of the region of validity of the Laplace-Poisson equations, and it may be useful to give here a short indication of a comparatively simple development of the equations (Ferguson, 1913).

Consider the pressure-excess at a point $P(x,y)$ in a large bubble flat at the vertex O (see figure 1). Obviously, if R_1 and R_2 are the principal radii of curvature at P,

$$g\rho y = \gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right), \quad \text{or} \quad \frac{y}{a^2} = \frac{1}{R_1} + \frac{1}{R_2}.$$

But $R_1 = \sec\phi/(d\phi/dx)$ and $R_2 = x/\sin\phi$, leading to

$$a^2 x \cos\phi \cdot \frac{d\phi}{dx} + a^2 \sin\phi = xy.$$

If we transfer the origin to O', and divide through by r, we arrive at an equation in which small terms occur with r in the denominator. Neglecting these terms, we easily find

$$y = 2a^2(1 - \cos\phi),$$

so that $\cos\phi = (2a^2 - y^2)/2a^2$ and $\sin\phi = y\sqrt{(4a^2 - y^2)}/2a^2$, the positive sign being the relevant one in our investigation.

If we insert these approximate values in the *small* terms of the original equation and integrate again, we obtain

$$2a^2(1 - \cos\phi) = y^2 + \frac{(4a^2 - y^2)^{3/2}}{3r} - \frac{8a^3}{3r}. \qquad \ldots\ldots(8)$$

The figure shows that when $y = h$, $\phi = \pi/2$, and, therefore,

$$h^2 = 2a^2 + \frac{2a^2}{3r}(4 - \sqrt{2}). \qquad \dots \dots (9)$$

When $y = k$, $\phi = \pi - \theta$, where θ is the contact angle, and

$$2a^2(1 + \cos\theta) = k^2 + \frac{(4a^2 - k^2)^{3/2}}{3r} - \frac{8a^3}{3r}, \qquad \dots \dots (10)$$

or

$$k^2 = 4a^2 \cos^2\theta/2 + \frac{8a^3}{3r}(1 - \sin^3\theta/2). \qquad \dots \dots (10\,a)$$

When r becomes indefinitely large, these reduce to the well-known simple forms

$$h^2 = 2a^2 \quad \text{and} \quad k^2 = 4a^2 \cos^2\theta/2. \qquad \dots \dots (11)$$

Equations (9), (10) and (10 a) are formally identical with the Poisson equations, and equation (9) is identical with equation (7) if we make a substitution equivalent to $h^2 = 2a^2$ in the small term of (9). The degree of approximation involved may be illustrated by considering a large bubble of water of *radius* 4 cm. If, as is not uncommonly the case, we use the simple formulae (11), we are neglecting a/r in comparison with unity. As we have seen, a for water may be taken as 0·27 cm., and a/r is therefore about 0·07; its neglect involves an error of the order of 7 per cent. If, with such a bubble, we use equations (9) and (10 a), we are neglecting a^2/r^2 in comparison with unity and the error involved is of the order of 0·5 per cent. Evidently, *with water*, a bubble of diameter 8 cm. is the smallest to which the Poisson equations may be safely applied. If the approximate value of a is not known for the substance under examination, a rough measurement of the bubble should be made, and its size adjusted so that h^2/r^2 is negligible in comparison with unity.

Magie (1888) was one of the first investigators to make systematic determinations of contact angles based on accurate measurements of large bubbles in which due account was taken of these correcting terms. He imprisoned a large bubble of air under the surface of a plano-concave lens immersed in a cell containing the liquid under test and, in interpreting his measurements, allowed for the effect of the curvature of the lens. He used the formulae just developed, and included a term which took account of the possible effect of the radius of curvature at the vertex of the bubble. He made measurements on bubbles with *diameters* ranging between 2·5 and 15 cm. Calculations were made of a^2, first from the h equation, and then from the k equation, assuming a zero contact angle. If any significant difference was noticed, the contact angle was then calculated.

Magie found zero contact angles with glass for methyl and ethyl alcohols, chloroform, formic acid and benzene. Finite contact angles were found for acetic acid (20°), turpentine (17°), petroleum (26°) and ether (16°). The figures for water pointed (doubtfully) to a small contact angle.* The method has

* In Magie's units, for one series $a_h{}^2 = 14{\cdot}99 \pm 0{\cdot}025$; $a_k{}^2 = 14{\cdot}41 \pm 0{\cdot}068$. For a second series, $a_h{}^2 = 14{\cdot}72 \pm 0{\cdot}018$; $a_k{}^2 = 14{\cdot}53 \pm 0{\cdot}022$.

been extensively used both for measurements of surface tension and of contact angle. A helpful description of the technique to be employed in measurements of sessile drops of mercury is given in Searle's *Experimental Physics* (1934).

Another method involving the simultaneous determination of γ and of $\cos\theta$ is based on a development of an experiment originally due to Sentis (1887). A thick-walled capillary tube is drawn out to a fine point at one end and is supported vertically so that it contains a thread of liquid of length h, part of the liquid forming a pendent drop at the lower end of the tube. Consideration of the pressures at A, B, C and D shows that

$$2\gamma/R + 2\gamma/r = g\rho h, \qquad \ldots\ldots(12)$$

where R and r are the *radii of curvature* of the surfaces at C and at A.

This equation is exact.

Now bring up to the tube a vessel containing some of the liquid under experiment, the vessel being supported on a table which may be raised or lowered (a suitably mounted spherometer serves very well). Raise the table until the surface of the liquid just touches the pendent drop, and take the spherometer reading. Raise the table further until the upper meniscus is restored to its original position in the tube, and again take the spherometer reading. The difference of these readings gives $(h - h')$.

From figure 2 (b),

$$2\gamma/r = g\rho h', \qquad \ldots\ldots(13)$$

and from (12) and (13)

$$2\gamma/R = g\rho(h - h'). \qquad \ldots\ldots(14)$$

This equation gives γ, independently of any knowledge of the contact angle.

So far Sentis.

If now we assume that the capillary is fine enough to justify putting $r' = r\cos\theta$ without sensible error, where r' is the internal radius of the tube at A, elimination of γ from (12) and (13) gives

$$\cos\theta \,.\, (h - h')/h' = r'/R, \qquad \ldots\ldots(15)$$

an equation for $\cos\theta$. It is not sufficiently exact in either of the equations (14) or (15) to identify R, the radius of curvature at the vertex of the drop, with R', the radius of the maximum horizontal section. It can easily be shown (Ferguson and Dowson, 1921) that, where $a^2 = \gamma/g\rho$, we can put

$$R = R'(1 - R'^2/6a^2)$$

if terms of the order R'^4/a^4 are negligible.

Hence it follows that, more accurately,

$$\cos\theta \,.\, \{(h - h')/h' - R'/3h'\} = r'/R'. \qquad \ldots\ldots(16)$$

There are certain experimental difficulties in this apparently simple experiment which will be discussed at length elsewhere.

Any pair of methods, one of which gives γ, the other $\gamma \cos \theta$, may be used to determine $\cos \theta$. It is advisable that the methods selected should be so chosen that the experiments can be carried out in rapid succession on one and the same specimen of liquid. Thus, a simple modification of the capillary-rise experiment consists in immersing a vertical thick-walled capillary in a liquid and measuring the pressure needed to hold the meniscus just at the lower end of the tube. This gives $\gamma \cos \theta$ (Ferguson and Hakes, 1929). If we now measure the pressure needed to detach a bubble of air from the lower end of the tube, we obtain a value for γ, and a comparison of the pressures, if we take due account of small corrections, serves to determine $\cos \theta$.

Bosanquet and Hartley (1921) determined the contact angle between wax and water by coating a capillary tube internally with a thin transparent layer of wax. This was accomplished by introducing a small quantity of wax into
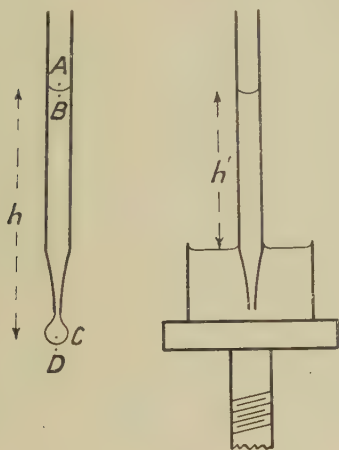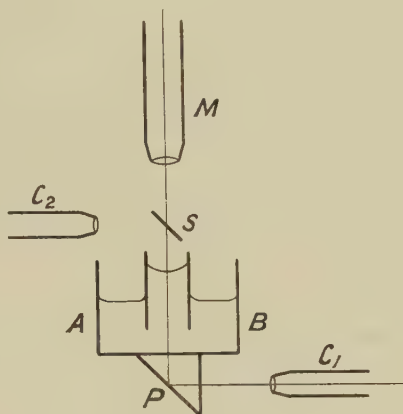
Figure 2.   Figure 3.

the tube, warming the tube and spinning it on a lathe while drawing a current of warm air through the tube. The capillary depression of water in the tube was measured, and the surface tension of water was taken as $73\cdot4$ dyne-cm.$^{-1}$ at $14°$ c. The mean value of θ was found to be $106°$ $57'$.

Anderson and Bowen (1916) have described a particularly neat method for the determination of $\cos \theta$. In the final form of the apparatus, a glass vessel AB with plane sides and base had cemented to its base a right-angled prism P. Parallel light from a collimator C_1 was reflected by the prism P along the axis of a tube dipping vertically into the liquid in AB, and the image formed by refraction at the meniscus was focused by means of a low-power microscope M. The radius of curvature (R) of the meniscus at the vertex is given by $R = (\mu - 1)v$. To determine v it is necessary to focus on the meniscus, and, to avoid this difficulty, parallel light from a second collimator C_2 is reflected on to the meniscus by a microscope slide-cover S, giving a reflected image at a distance $R/2$ from the

meniscus. Hence, if d be the difference of the microscope readings for the reflected and refracted images, $R = 2(\mu - 1)d/(\mu + 1)$.

If experiments are carried out with tubes of different radii (r), a plot of r as abscissa against R as ordinate will give a curve which approaches the origin at $\tan^{-1}(\cos\theta)$. For water, glycerine, olive oil and turpentine the slope of the curves at the origin was 45°, pointing to a zero contact angle. For mercury, a contact angle of 139° was found.

The march of R with r is illustrated by the figures for olive oil and for mercury:

Olive oil	Mercury
r: 0·328, 0·222, 0·155, 0·045	r: 0·381, 0·215, 0·156, 0·056
R : 0·460, 0·267, 0·162, 0·045	R : 0·822, 0·316, 0·214, 0·074

The method is simple and trustworthy and might well be more widely used.

The same end may be attained by measuring the *height* of the meniscus in a narrow capillary. Richards and Coombs (1915) have done this by placing a screen with a horizontal edge behind the tube, raising the screen until its edge is tangential to the vertex of the meniscus, and then raising it further until the edge is just on the line of contact. In all intermediate positions the edge appears distorted, and the initial and final settings seem to be quite sharp. Thus for a tube of radius 0·20 mm. the meniscus height (Y) was 0·20 mm.; for a tube of radius 1·01 mm. the corresponding meniscus height was 0·964 mm. This points to a zero contact angle, inasmuch as, to the order r^2/a^2, the height of such a meniscus is given by

$$Y = r - (r^3 \log_e 2)/3a^2. \qquad \ldots\ldots(17)$$

The equations for meniscus height for a liquid of finite contact angle are clumsy but not very difficult to handle. Thus, it can easily be shown (Minchin, 1892) that, to the approximation considered,

$$Y = c - \sqrt{(c^2 - r^2)} + \frac{c^3}{3a^2} \log_e \frac{c + \sqrt{c^2 - r^2}}{2c}, \qquad \ldots\ldots(18)$$

where the constant c is given by

$$c = r \sec\theta \left\{ 1 - \frac{r^2}{3a^2} \cdot \frac{\sin^2\theta(1 - \sin\theta)}{\cos^4\theta} \right\}. \qquad \ldots\ldots(19)$$

Evidently as r decreases, Y approaches the limit

$$Y = r \sec\theta - r \tan\theta,$$

as is otherwise obvious; hence, if values of Y and of r are measured under conditions such that terms of the order r^2/a^2 are negligible, θ is easily determined.

If the contact angle is zero $c = r$ without neglect of the terms in r^2/a^2. Hence equation (17).

But direct determinations of θ are perhaps preferable, though even here the simple technique of the methods usually adopted presents difficulties connected with the " hysteresis " of the contact angle. The simplest modes of

attack on the problem are by pouring the liquid into a spherical receptacle, or immersing a solid sphere in the liquid, to such a depth that the liquid surface remains plane right up to its line of contact with the solid, by dipping a plane surface of the solid in the liquid and tilting the plane until the liquid meets the solid without any sign of curvature, by immersing a solid cylinder in the liquid to a suitable depth, or by forming small bubbles or drops on the horizontal surface of the solid and making direct measurements on them.

Bosanquet and Hartley (1921) formed plates of paraffin wax and of azobenzene on glass, mounted the plates on a vertical divided circle placed in water, and tilted the system until the water surface was plane. For paraffin wax they found $\theta = 106° 28'$, for azobenzene $\theta = 77° 20'$.

Nietz (1928) has developed an apparatus in which a disk with its plane vertical is mounted on the chuck of a jeweller's lathe so that it may be rotated about its horizontal central axis. A clamp, whose jaws are some little distance in front of the plane of the disk, is attached eccentrically to the disk and carries a microscope slide covered with the solid under test, which dips into the liquid contained in a rectangular glass jar placed in front of the disk. A piece of glass ruled with horizontal black lines at intervals of about 3 mm. is cemented to the rear surface of the jar, and the planeness of the surface up to the line of contact is determined by watching the image of the lines reflected from the underside of the liquid-to-air interface. The height of the liquid is adjusted until the axis of rotation of the disk is in the surface of the liquid. For specially purified paraffin wax the author finds a contact angle of $109° \pm 30'$.

Sumner (1937) has described a piece of apparatus designed on similar lines, with the additional advantage that the plate, after clamping, may be raised or lowered at will so that advancing or receding contact angles may be readily determined. The author confirms the large differences between these angles obtained in the earlier experiments by Adam and Morrell (1934). Thus, for paraffin wax, he obtains a mean advancing angle of $107° 30'$; a mean receding angle of $95°$.

Adam and Shute (1937) have devised a particularly neat modification of the tilting-plate method suited to the determination of the contact angles of liquids with wires or textile fibres. The wire or fibre is gripped by two surgical bulldog clips which are soldered to the ends of a pair of spring box compasses after removal of the points. The fibre can thus be made taut by moving the screw of the compasses. The holder is attached to a brass ring which can be rotated in a vertical plane, and the whole system can be moved up and down by means of a vertical screw. The manner of use of the apparatus demands little explanation. The fibre is viewed through a low-power horizontal microscope. Contact angles can be estimated to within five degrees, and the apparatus can be used to measure interfacial contact angles.

Ablett (1923) first developed the cylinder method. A cylinder of diameter d is placed in a rectangular glass tank with its axis horizontal. The cylinder is

coated with the substance under investigation, and water is fed into the tank until the surface of the water is plane right up to the line of contact with the cylinder. If the cylinder is now immersed to a depth h, obviously $\cos \theta = (2h/d) - 1$.

The cylinder is now slowly rotated by a motor and reduction gear, the belt which finally transmits power to the cylinder being a closely wound helical spring.   By rotating the cylinder, first clockwise, then anti-clockwise, it is possible to find values for advancing and receding contact angles for different peripheral speeds of the cylinder.   The limits of peripheral speeds lay between 0·13 and 3·9 mm./sec.   With increasing speed, θ_1 increases and θ_2 diminishes in such a way that $2\theta = \theta_1 + \theta_2$, where θ is the equilibrium value.   For peripheral speeds greater than 0·44 mm./sec., θ_1 and θ_2 remain sensibly constant.   In a later communication to the symposium on Wetting and Detergency, Ablett (1937) shows that the results are better represented by the equation $2 \cos \theta = \cos \theta_1 + \cos \theta_2$, which agrees with the experimental results very closely.   For peripheral speeds greater than 0·44 mm./sec. he finds $\theta_1 = 113° 9'$, $\theta_2 = 96° 20'$, and the equilibrium value $104° 34'$.   The figures are subject to a probable error of $\pm 5'$.

Taggart, Taylor and Ince (1930) and Wark and Cox (1934) have measured contact angles directly by forming an air bubble in a liquid between the lower end of a vertical tube and the surface under investigation, the liquid being contained in a cell with parallel sides of optical glass.   The tube is about 3 mm. in diameter, and the bubble has a diameter of about 5 mm.   A magnified image of the bubble is projected on to a screen, and the contact angle directly read off.   According to Wark and Cox, hysteresis effects are due to friction and tend to disappear with increasing polish of the surface.

Mack (1936) has also determined contact angles from measurements made on small bubbles and drops.   This first paper deals with the spheroidal segment method for acute angles, and the author points out that the method has some advantages over those methods which measure the angle directly from a single observation, inasmuch as the value given by this method is " the integral of the sum of all the separate angles along the circumference of the drop ".

The solid to be investigated is embedded on a paraffined glass plate.   The liquid is placed in a short length of glass tubing, one end of which is drawn out to a fine point.   The tube is held vertically, and drops form at the lower end of the tube.   Drops of a constant and reproducible size are detached by touching the surface with the tip at definite time intervals.   The volume of the liquid for a given number of drops is measured from observation of the lowering of the level of the liquid in the capillary.   Hence the volume (V) of each drop is known. The diameter (x) of each drop is measured in the ocular of a low-power microscope. If h is the height of a drop, the angle between the horizontal plane through the base of the drop and the tangent to the spherical surface at the point of contact is

$$\theta = 2 \tan^{-1}(h/x).$$

x is easily measured; h is smaller and more difficult to measure. But we have

$$h^3 + 3hx^2 = 6(V/\pi),$$

which may be written

$$(\pi/6)(h/x)^3 + (\pi/2)(h/x) = V/x^3.$$

A table is drawn up once for all, giving corresponding values of the non-dimensional quantities h/x and V/x^3. Knowing V and x^3 for any one drop, we obtain h from the table, and therefore θ.

In a second paper by Mack and Lee (1936) the theory is extended to a consideration of the sessile drop with obtuse angles. Extensive use is made of the tables compiled by Bashforth and Adams (1883).

There is, then, no lack of methods for the determination of contact angles, and a consideration of the relative merits of these methods is a matter of considerable interest. This paper is an attempt to furnish material to that end.

But, it may very well be asked, having obtained your contact angle, what do you do with it? Some aspects of the answer to that question are dealt with in the introduction to this article. Further information may be found in the record of the conference on Wetting and Detergency and in the books by Adam, Burdon and Wark mentioned in the appended list of references.

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DISCUSSION

Dr. G. MACDOUGALL. Dr. Ockrent and I have been measuring contact angles as a method of investigating the lithographic printing process.

A drop of liquid is placed on a flat horizontal plate and illuminated at grazing incidence by a parallel beam of light. An image of the drop (magnification about 80 diameters) is thrown on a screen bearing a divided scale. The tangent at the point of contact of the liquid and solid is obtained by suitable manipulation of a fine hair-line photographed on a glass slip. Results may be reproduced to within 0°·5 or less. The screen is a photographic plate with barium sulphate precipitated in the emulsion. The flat, horizontal plate is mounted on a stage which can be traversed across the field of view and which also revolves around the axis of the microscope. On tilting the plate, the contact angles of the liquid drop change. With systems such as water on paraffin wax and mercury on glass the contact angle at the lower edge of the drop remains constant at the same value as the drop on the horizontal plate. The angle at the upper edge of the drop decreases progressively as the plate is tilted until a point is reached when the drop starts to slide down the inclined plate. We find that the magnitude of the contact angle corresponding to the point of incipient sliding is reproducible and independent of the size of the drop and consequently of the angle of tilt at which sliding occurs. The drop therefore exhibits two constant and reproducible contact angles corresponding to advancing and receding menisci. We have no evidence that a liquid normally assumes a characteristic equilibrium angle which is intermediate between the advancing and receding angles. In our view, all contact angles smaller than the advancing angle and greater than the receding angle can under certain circumstances correspond to equilibrium of a liquid resting on a solid surface.

If a drop of water, for example, resting on a horizontal paraffin-wax surface is allowed to evaporate, the contact angle diminishes, the drop remaining symmetrical. If the plate is now tilted, the contact angle at the lower edge increases and that at the upper edge decreases until the drop starts to slide, by which time the contact angles have assumed the values of the advancing and receding angles. Drops of liquids placed on surfaces such as stearic acid or tristearin are initially symmetrical and have contact angles which we find are not reproducible. Nevertheless, when the stage is tilted sufficiently for sliding to begin, we have observed that the contact angles are then constant and reproducible as before. Materials which do not show a constant initial contact-angle having the same magnitude as the advancing angle are of the type which have a polar group attached to the end of a

long hydrocarbon chain. We have observed that the magnitude of the advancing angle and the difference between the cosines of the receding and advancing angles place solids and liquids in the order which would be expected from a consideration of the orientation and polarities of the molecules at the solid-liquid interface.

We have extended this method to the measurement of interfacial contact-angles between two liquid phases and a solid phase. A solid flat plate is placed in a flat-sided glass cell and immersed in a liquid. A drop of the second liquid is formed on the solid surface by means of a capillary pipette. In this case, also, the advancing and receding angles were constant and reproducible. We have been able to show that the receding and advancing angles observed with a drop of liquid A in liquid B are the same as the supplements of the advancing and receding angles respectively observed with drops of liquid B in liquid A. We find that interfacial angles are much more sensitive to the presence of adsorbed films on the solid surface than are contact angles.

Dr. K. G. A. PANKHURST. I should like to ask Dr. Macdougall whether his estimate of one-half degree as the accuracy with which he was able to measure contact angles was also a measure of the reproducibility of the results obtained. For example, in determining the contact angle between paraffin wax and water, were measurements made with different samples of paraffin wax all within the limit of this estimate? I ask this question because it has been my experience that, using the " plate " method, contact-angle determinations are seldom reproducible to less than 5°, and in some cases, especially with set gelatin layers and water, the figure was as high as 10 to 15°.

Mr. L. V. CHILTON. I should like to put in a plea that the nature of the solid surface involved in contact-angle discussions should always be mentioned. Many of the solid surfaces of interest in industry behave very differently from those of glass and of paraffin wax, to which the bulk of published data refer. This has some important consequences, viz. (1) the published methods for determining contact angle are often inapplicable, (2) some of the conclusions published as applying generally to contact angles are no longer valid. These two points may be well illustrated by reference to the wetting of gelatin gels by aqueous solutions. These gels absorb water and do not appear to exhibit a receding contact angle. Their advancing contact angle, moreover, does not increase to a steady value with increasing rate of advance, as would be expected from Ablett's rotating-cylinder observations with paraffin-wax surfaces. Indeed, in the system water-gelatin gel, as the rate of advance is increased the advancing contact angle progressively increases until it reaches 180° and wetting of the solid phase no longer occurs. The precise magnitudes involved depend on many factors, but in a typical case where the contact angle at rest is about 90°, increase of the " advancing " angle to 180° may be reached at a speed of advance of the order of 5 cm./sec.

Dr. A. E. BATE.   If a very large bubble is formed in a liquid of density ρ beneath a flat horizontal plate, the relationship between the surface tension T, angle of contact γ and the depth d of the bubble is given by

$$T + T \cos \gamma = d^2 g \rho / 2.$$

When the liquid is placed on the plate to form a drop of similar extent and of height h, the expression is

$$T - T \cos \gamma = h^2 g \rho / 2.$$

Adding the expressions, we have

$$2T = (d^2 + h^2) g \rho / 2.$$

Subtracting and substituting for T,

$$\cos \gamma = \frac{d^2 - h^2}{d^2 + h^2} .$$

Thus T may be obtained independently of γ, and γ may be obtained independently of T.

In practice, however, the bubbles and drops are of finite size, and it is necessary to modify the expressions in the way Prof. Ferguson has indicated.

[The expressions, and details of the experiments, are omitted, as they have been published since the date of the lecture. See this volume, p. 403.—EDITOR.]

Contact angles of several degrees were found for all the liquids used, including water, in the course of what must be regarded as preliminary experiments.   This may be due to the glass plate giving different values from the tubular glass, where, in the case of water, Professor Ferguson has stated that the angle is zero.   On the other hand, it is not unlikely that other workers have not noticed the existence of a contact angle owing to the smallness of the error involved in assuming it to be zero.   For example, for an angle of $5°$, $\cos 5°$ is $0 \cdot 9962$, which means an error of $0 \cdot 38 \%$ when $\cos 5°$ is replaced by $\cos 0$.

SUPERCOOLED SILICATES AND THEIR IMPORTANCE IN CONSIDERATIONS OF THE LIQUID STATE

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ABSTRACT.   A study of the properties of crystallization, viscosity, electrical conductivity and surface tension shows that silicate glasses are supercooled liquids and may be regarded as solutions, the constituents of which are associated to a greater or lesser degree, depending on composition and temperature.   Recent researches on the

structure of glasses by x-ray methods indicate that it is typical of the liquid state. Glass at room temperatures possesses a static structure as opposed to the dynamic ever-changing configuration of the particles of a normal liquid, and on this account simple glasses may prove to be of great value in the further elucidation and the provision of an adequate theory of the structure of liquids.

§1. INTRODUCTION

ONE of the foremost problems in modern theoretical physics is the provision of an adequate theory of the constitution of the liquid state.* Such a theory must correlate all the properties of the liquid state with its atomic or molecular structure and must be in accord with known chemical facts. In the last generation much research has been directed towards this end, yet the position is only a little clearer than when W. E. S. Turner (1915) wrote of molecular complexity in the liquid state, " the determination of the molecular condition of matter in any condition other than the diluted state is attended at present with very considerable difficulties .... with one or two exceptions, indeed, all the methods available are empirical ".

From Trouton's rule to the order-disorder theory (J. E. Lennard-Jones and A. F. Devonshire, 1939 a and b) and the theories of holes (R. Fürth, 1940 a and b) is a long and tortuous path. Yet attempts have been made, not unsuccessfully so far as simple unassociated liquids are concerned, to express such properties of the liquid state as viscosity, density and surface tension in terms of fundamental atomic or molecular values. Such equations have value in that they have some fundamental significance, but it is still true that there is as yet no completely satisfactory theory of the structure of the simplest unassociated liquid.

The classical chemical conception of association, a process akin to chemical reaction except that it takes place between similar and not dissimilar particles, brings with it further problems before we can formulate a theory of the structure of a salt solution and finally obtain a satisfying answer to that troubled question in which the writer is most interested, namely, " the constitution of glasses ", the most supercooled of all liquids. The glasses of commerce are sufficiently stable in their metastable condition for their physical and chemical properties to outclass those of many crystalline solids. It is this very great degree of supercooling which may well be the means by which a clearer insight into liquid constitution may be obtained, in spite of the highly associated condition of glasses.

That inorganic glasses and those organic glasses of the thermoplastic type at room temperatures are simply undercooled solutions and not, as some would claim, a special or fourth state of matter (E. Berger, 1931, 1932 ; O. Knapp, 1930), appears to the writer to be almost axiomatic, yet it has been the source of much polemical discussion (*J. Soc. Glass Tech.* 1927 ; see also E. Preston and W. E. S. Turner, 1934 a). It is the purpose of this paper to point out that as regards

* For a recent statement of the position, see the joint discussion by the Physical Society and the Cambridge Philosophical Society, *Proc. Phys. Soc.* 1940, **52**, 729–69, papers by J. E. Lennard-Jones, E. N. da C. Andrade, A. Ferguson, J. Corner and R. Fürth.

the properties of viscosity, electrical conductivity, surface tension, volatilization and crystallization, such glasses behave in a manner completely characteristic of the liquid state, the differences being of degree only and not of kind, and to indicate that glasses may prove to be useful tools in the elucidation of the problem of the liquid state.

§ 2. GLASS AS A SUPERCOOLED LIQUID

The equilibrium diagrams of many silicate systems are now comparatively well known: indeed, F. P. Hall and H. Insley (1933, 1938) have collected together 332 such phase-equilibrium diagrams of importance in the glass, refractory and ceramic industries. Our knowledge is probably most complete regarding the system of first importance in glass technology, namely, the soda-lime-silica system (G. W. Morey, 1930). The attainment of equilibrium in glasses of this system by reheating at temperatures below the liquidus temperature of the particular composition investigated results in the crystallization of the equilibrium constituents. A crystal growth-temperature curve may be constructed which is entirely characteristic of crystallization from a supercooled solution. The form of such curves was first studied at length by G. Tammann (1903, 1933) and is
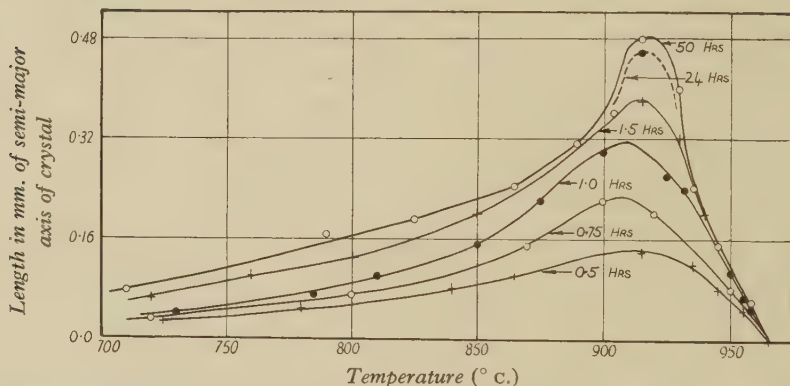
Figure 1. Crystal growth of devitrite ($No_2O . 3CaO . 6SiO_2$), the primary crystalline phase in a sheet-glass composition at different temperatures determined by the gradient method after 0·5, 0·75, 1·0, 1·5, 24, and 50 hours heating respectively.

illustrated by figure 1, which shows {crystal-growth, temperature} curves for a sheet-glass composition examined by the writer (E. Preston, 1940) for the crystallization of the primary crystalline phase, devitrite, $Na_2O . 3CaO . 6SiO_2$.

The search for an empirical equation to represent the {crystal growth, temperature} curves led the writer to the general conclusion that in supercooled liquids of this type, crystal growth was inversely proportional to the viscosity of the medium in which the crystals grow, directly proportional to the rate of diffusion through the medium of essential crystal-forming constituents, and directly proportional to the degree of supercooling as characterized by the temperature interval below the liquidus temperature at which crystallization takes place.

Thus, r (rate of crystal growth)

$$= k \frac{1}{\text{viscosity}} \text{ (rate of diffusion) (degree of supercooling).}$$

Unfortunately there are as yet no data for the diffusion processes in glasses, and it has to be assumed that such diffusion for a given constituent will be proportional to the mobility of the liquid. Since mobility is the inverse of viscosity, we have

$$r = K(1/\eta)^2(T_{\text{liq.}} - T),$$

where $\eta =$ viscosity, $T =$ absolute temperature.

For the glass for which results have been given in figure 1, to a first approximation,

$$\eta = c e^{12,000/T},$$

and as shown in figure 2, a plot of the equation,

$$r = K e^{-24,000/T}(T_{\text{liq.}} - T)$$
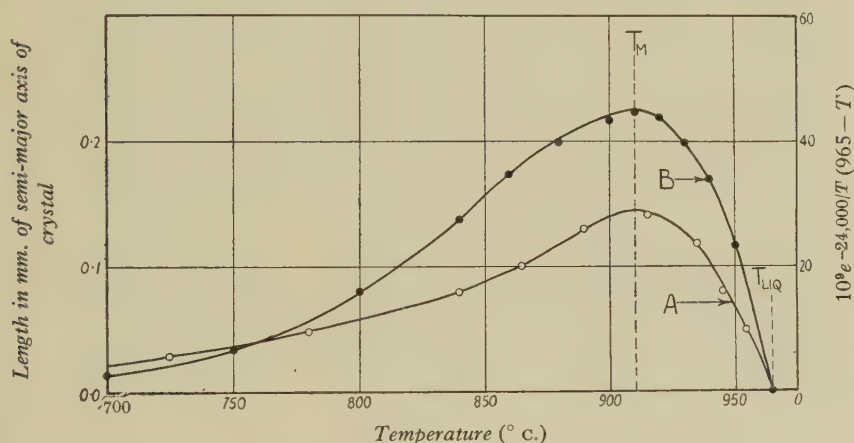
Figure 2. Curve A: Relation between crystal size and temperature for the initial heating period of 0·5 hr. for the crystallization of devitrite from a sheet-glass composition. Curve B Variation with temperature of the expression $e^{-24,000/T}(965 - T)$.

does satisfactorily reproduce the {crystal growth, temperature} curves during the early period of crystal growth in which growth is almost linear with time, and the temperature of maximum crystal growth is correctly given.

It cannot be said that the above formula has any fundamental significance other than that the assumptions involved in it appear to be reasonable, and that the first and third factors are capable of experimental verification. It may be, however, that it is capable of general application to the case of supercooled solutions. Although the equation has been derived (E. Preston, 1940, 1941) by a method fundamentally different from that of Tammann, the only difference between curves such as those of figures 1 and 2 and those given by him for organic and inorganic solutions is the vastly longer times required for the crystals to grow and the very much greater degree of supercooling possible. Thus, in the

writer's view, all glasses are correctly regarded as liquids in which the process of cooling has been too rapid to allow crystallization to proceed when the temperature has fallen below the liquidus temperature, and ultimately crystallization becomes impossible in any realizable time because of the very great viscosity of the glass and the difficulty of diffusion of constituents within it.   On maintaining such a supercooled liquid at the requisite temperature, or by sufficiently slow initial cooling, the course of separation from the saturated solution of primary crystalline phase and binary eutectic may readily be followed (E. Preston, 1940).

Figure 3.   Crystallization of binary eutectic of devitrite-cristobalite in a sheet glass composition, ×800.   (Devitrite-monoclinic, long needles, top left.   Cristobalite-cubic, small dendrites.)

In general, in a three-component glass system the ternary eutectic does not separate so readily, because of the lower temperature involved.

On this view alone we should expect a glass to retain a structure akin to that of the liquid state, and modern researches tend to show that this is so.   The devitrification of glass, i.e., the separation of those crystalline products characterized by the equilibrium diagram for the system from a saturated solution, is ample demonstration of its supercooled nature.   An example of the devitrification of a devitrite-cristobalite eutectic is shown in figure 3.

§ 3. GLASS AS AN ASSOCIATED LIQUID: THE IMPORTANCE OF VISCOSITY

Classical methods for the establishment of the existence of association in liquids, although in the main of a quasi-empirical nature, have been of immense value and, in general, the conclusions remain unchallenged.   Such a method was first applied to inorganic soda-lime-silica glasses by W. E. S. Turner (1925),

who made use of the Ramsay and Shields surface-tension equation. The results showed that by all previous standards the glasses were to be regarded as of high molecular weight.

In recent years increasing attention has been given to the finding of a satisfactory relationship between viscosity and temperature for liquids. For simple unassociated liquids the formulae deduced are all of the type

$$\eta = ke^{A/T} = Ke^{-ML/RT}, \qquad \ldots\ldots(1)$$

and in general from the slope of the $\{\log \eta,\ 1/T\}$ curves a satisfactory estimate may be made of the latent heat of fusion. For example, F. W. Preston (1932) by this method obtained 31·4 and 3·1 cal./g. respectively for benzene and mercury, the accepted values being 30·6 and 2·82 cal./g. Similar calculations by J. N. Friend (1935) showed good agreement in ten unassociated liquids examined by him. In his recent paper E. N. da C. Andrade (1940) would appear to regard the linearity of a $\{\log \eta,\ 1/T\}$ plot as " always a good test with simple liquids ."

In those cases where association is known to occur, such as the case of water, i.e., where it has been deduced by other methods, the value of A in the viscosity equation does not remain constant throughout the temperature range, but the results are satisfactorily accounted for by supposing association to occur with consequent variation in molecular weight at different temperatures. Andrade (1930) has given the following equation for associated liquids,

$$\eta = A(1 + ae^{-\beta/T})e^{b/T}, \qquad \ldots\ldots(2)$$

containing two energy terms representing the heat of fusion and the heat of association, and this equation is applicable also to the viscosity-temperature relationships of glasses (S. C. Waterton, 1932).

Viscosity measurements have been employed by many other workers as indicators of association, notably by Friend (1935), who used the empirical observation that over a considerable range of temperature in the neighbourhood of the boiling-points of pure unassociated liquids, the product of viscosity and the square root of the vapour pressure rose linearly with absolute temperature according to the expression

$$\frac{\eta p^{\frac{1}{2}}}{T - A} = B,$$

but that associated liquids did not conform to this rule. Friend reduced this to

$$\log p_2/p_1 = 4 \log\left(\frac{T_2 - A}{T_1 - A}\right)$$
$$= 4 \log \eta_1/\eta_2, \qquad \ldots\ldots(3)$$

since η_1/η_2 did not differ appreciably from $((T_2 - A)/(T_1 - A))$ in the region of the boiling point. It may be pointed out here that a similar relation can be shown to be true for certain glasses at high temperature : for example, a pure soda-silica glass containing 49 per cent Na_2O, for which

$$\log \eta_1/\eta_2 = K \log p_2/p_1,$$

in which p_1 and p_2 are the partial pressures of the volatilizing alkali at given temperatures and η_1 and η_2 the viscosities at the same temperatures.

Combining equation (3) with the Clausius-Clapeyron equation, Friend arrived at the expression

$$\frac{\log(\eta_1/\eta_2)}{(1/T_1 - 1/T_2)} = C, \qquad \qquad \dots\dots(4)$$

a constant for unassociated liquids, and held the opinion that this product should be a sensitive indicator of association. Thus, by a somewhat circuitous route, we arrive again at the slope of the {log η, $1/T$} curves.

A little later, D. B. Macleod (1936) developed an equation in which the viscosity of a liquid was assumed to be proportional to its internal pressure, $\pi_0 e^{C_1/Tv}$ and to its " effective " molecular weight, $M_0 e^{C_1/Tv}$, and inversely proportional to the absolute temperature. The significance of Macleod's treatment is that the internal pressure of a liquid was assumed to create a temporary degree of association, probably the normal and inevitable condition of a liquid, and the divergence of liquids from generalized laws was held to be due to such varying degrees of association.

In A. G. Ward's (1937) derivation of a viscosity-temperature equation, the number of ions or molecules having sufficient energy to bring about a configurational change due to viscous shear was given by the Boltzmann law as proportional to $e^{-B/RT}$, and the following equation obtained :

$$\eta = A(T)e^{B(T)/RT}, \qquad \qquad \dots\dots(5)$$

in which A and B are both functions of temperature. J. D. Bernal (1937) had shown that in those liquids having directional forces, the co-ordination increased with temperature, whilst in liquids possessing no directional forces it remained constant, and Ward considered that a change from a low to a higher co-ordination rendered the configurational changes easier to bring about since the binding in any direction was then weaker. In agreement with this, the value of B decreased with increasing temperature, a striking example being fused boric oxide. It may be noted that B_2O_3 has probably never yet been obtained as a crystalline solid, but always as a glass.

It would seem that at moderately high temperatures, particularly in the range between the softening point and the liquidus temperature, glasses are liquids associated to varying degrees, for the plot of log η against $1/T$ is not linear. When viscosities of the order of 10^{12} or 10^{13} poises have been reached, corresponding in the normal soda-lime-silica glass to a temperature of about 800° K., the degree of association appears to become constant, and at lower temperatures the glass behaves as a non-associated liquid, the plot of log η against $1/T$ having become linear within experimental error, i.e., the factor A, equation (1), has become sensibly constant, indicating a constant degree of association.

Consideration along these lines led the writer with E. Seddon (1937) to arrive at an effective molecular weight for a certain soda-lime-silica glass of not less than

1000 at 1400° c., and not less than 3000 at 500° c. In this glass the primary crystalline phase was devitrite * $Na_2O.3CaO.6SiO_2$, of simplest molecular weight 596, and a very broad view of the association process may be obtained in terms of the following chemical change :

$$(Na_2O.3CaO.6SiO_2)_2 \underset{1400°}{\overset{}{\rightleftharpoons}} (Na_2O.3CaO.6SiO_2)_6.$$
$$\hspace{4cm} 500°$$

It is interesting to note here that in the field of glass technology P. Zulkowski (1899, 1900) forty years ago was led to the postulation of complexes of 36 SiO_2 in solid glasses from purely chemical considerations of the relative stabilities of the many glasses analysed by him. Other estimates of the effective molecular weights of glasses include those of P. Gilard and L. Dubrul (1936), who obtained values for a soda-lime-silica glass of 4410 at 1300° c., and 74 600 at 500° c. ; and those of M. P. Volarovitch and A. A. Leontieva (1937), who deduced that fused silica glass at 1250° c. contained aggregates of 540 SiO_2 molecules, and only 40 SiO_2 molecules at 1380° c. ; and for boric oxide the number of B_2O_3 molecules in individual aggregates varied from 18 at high temperatures to 163 at 260° c.

Andrade considers any explanation of viscosity based on diffusion or atom or molecule migration from one layer to another as unsatisfactory. With this view the present writer is in entire agreement. Macroscopic viscosity must always be regarded as a function of molecular size, and the movement of a molecule or layer of molecules relative to the adjacent molecule or layer, irrespective of the actual conception of what constitutes the " molecules." From fundamental considerations J. Frenkel (1926, 1927) derived the expression

$$\eta = \frac{\tau_0}{2\pi a \delta^2} . kT . e^{E\eta/kT}, \qquad \qquad \dots\dots(6)$$

in which τ_0 is the period of oscillation of a particle of the liquid about a temporary position of equilibrium, E_η the energy required to move the particle from one equilibrium position to another, δ the average distance between neighbouring particles, and α the radius of the particle (presumed spherical for simplicity). This mode of representing viscosity is analogous to the deformation of crystalline metals, which is known to proceed by slip along the most highly stressed crystal plane in the direction of the line of most highly stressed atoms. The slip proceeds from one position to another, each increment of slip being equal to the distance between adjacent atoms, so that they always occupy equivalent places in the crystal lattice and the crystal structure is at all times maintained.

In Frenkel's derivation, the expression

$$\frac{\tau_0}{2\pi a \delta^2} . k$$

is constant for unassociated liquids, and we have,

$$\eta = CTe^{E\eta/kT}, \qquad \qquad \dots\dots(7)$$

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* For an account of the properties, identification and examples of the crystalline products commonly found as devitrification products in commercial glass compositions see E. Preston and A. J. Holland (1937, 1938).

in which CT takes the place of the coefficient A in the Andrade equation. For associated liquids it is readily seen that the values of τ_0, α, and δ will be dependent upon molecular size, as also will the value of E .

The writer with E. Seddon (1937) has utilized Frenkel's equation and applied it to glasses, and the extent of variation of E_η with temperature has been indicated. At a later date, Seddon (1939) preferred the representation of values of the quantity $\tau_0/\alpha\delta^2$ as a function of temperature for glasses and other liquids as an indication of particle or " cluster " size. This quantity varied by as much as 10^{-30} to 10^{10} in certain cases examined by Seddon, though it is difficult to conceive of an increase in particle size of such magnitude (10^{40}). Frenkel himself indicated that it is $1/\alpha\delta^2$, which is approximately equal to the number, n, of particles in unit volume of the liquid. It may be noted that the quantity $kT/\alpha\delta^2 = nkT$ is equivalent to the pressure which, by the kinetic theory, these particles would exert
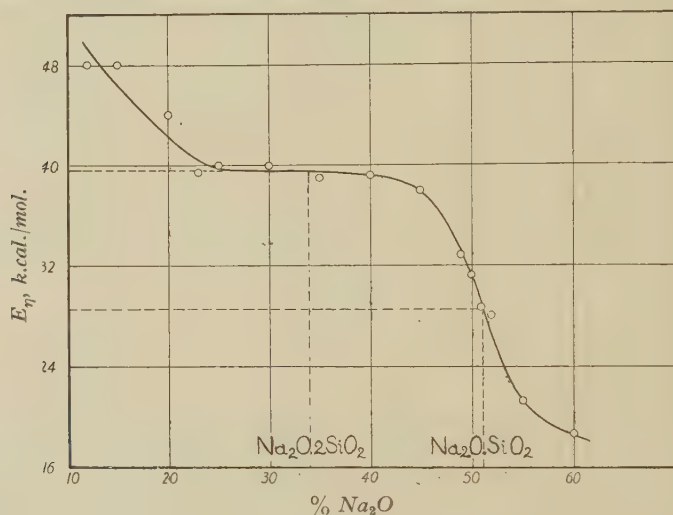
Figure 4. The {internal energy, composition} relationship for the soda-silica glasses.

if they formed a gas, and thus again we have the conception of an internal pressure in liquids.

To the writer's mind a convincing demonstration of the dependence of viscosity on particle size is given by figure 4, which shows values of E_η for a series of soda-silica glasses calculated from the viscosity determinations of G. Heidt-kamp and K. Endell (1936). If it be assumed that the degree of association in these glasses does not differ widely from one glass to another at the same temperature, then the ratio of the energy values at the compound compositions $Na_2O \cdot 2SiO_2$ and $Na_2O \cdot SiO_2$ are approximately in the same ratios as the simplest molecular weights of the compounds.

Ratios of the molecular weights $= 182/122$, or approximately $1 \cdot 5$.
Ratios of the internal energies $= 39 \cdot 5/28 \cdot 5$, or approximately $1 \cdot 4$.

This indicates a similarity between inorganic glasses and many organic substances, for which viscosity measurements have long been employed as a criterion of molecular size, as, for example, in the cellulose derivatives. In such cases H. Staudinger has made much use of the equation

$$\eta = K_m C M, \qquad \dots\dots(8)$$

in which K_m is a constant characteristic of each polymer, C the concentration, and M the molecular weight of the cellulose derivative in an organic solvent. By this means Staudinger found that the constituent molecules of the thermo-plastic organic glass, polystyrene, consisted of chains of from 20 to 6000 styrene units. It will be noted that the molecular weights deduced are of the same order as those for inorganic glasses at high temperatures and that the viscosities are comparable. In the aliphatic alcohols, which are also capable of forming glasses by sufficiently strong supercooling, a similar relation may be found between E_η and molecular size. The data of the following table have been collected together by Seddon (1939), who has refuted the idea of the presence of chemical compounds in glasses.

Table 1. Relation between E_η and chain.length
for aliphatic alcohols

Alcohol	Chain length by x-ray measurements	Ratio of chain lengths	E_η at 0° C.	Ratio of E_η
$CH_3 . OH$	$l_m = 4.3$ A.		$E_m = 3.0$	
		$l_e/l_m = 1.33$		$E_e/E_m = 1.22$
$C_2H_5 . OH$	$l_e = 5.7$		$E_e = 3.65$	
		$l_p/l_m = 1.60$		$E_p/E_m = 1.53$
$C_3H_7 . OH$	$l_p = 6.9$		$E_p = 4.6$	
		$l_b/l_m = 1.84$		$E_b/E_m = 1.72$
$C_4H_9 . OH$	$l_b = 7.9$		$E_b = 5.15$	

It will be noted that each addition of CH_2 increases the chain length by approximately 1.2 A., and the E_η values by approximately 0.7 kilo-calories, and it should be possible to calculate with fair accuracy the viscosities of the higher alcohols of the series. The chain length of such compounds is surely related to the molecular weight. If this is true for the organic alcohol glasses there seems to be no reason to adopt other views in considering the chemical constitution of inorganic silicate glasses.

Whether we abandon for ever classical chemical ideas of association and dissociation matters not. All the evidence points to the fact that glasses, which are undoubtedly true liquids above their respective liquidus temperatures, consist of relatively large particles or groups of atoms increasing in average size as the temperature falls until free movement is so restricted that at all lower temperatures the effective particle size remains appreciably constant. Such a temperature is frequently described by glass technologists as the " softening

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point " or " aggregation point ", and is characteristic of all glass-forming substances.

§4. GLASS IN THE LIQUID STATE

At temperatures above their respective liquidus temperatures all glasses, although viscous (the average commercial soda-lime-silica glass has a viscosity of about 200 poises at 1400° c.), are in the true liquid condition and their properties are similar to those of other liquids stable at room temperatures and follow the same laws. Brief mention only will be made of the properties of evaporation of volatile constituents, electrical resistivity, and surface tension. It is worthy of note that in this temperature region the degree of association or, if it is preferred, the degree of aggregation again becomes appreciably constant, and in general
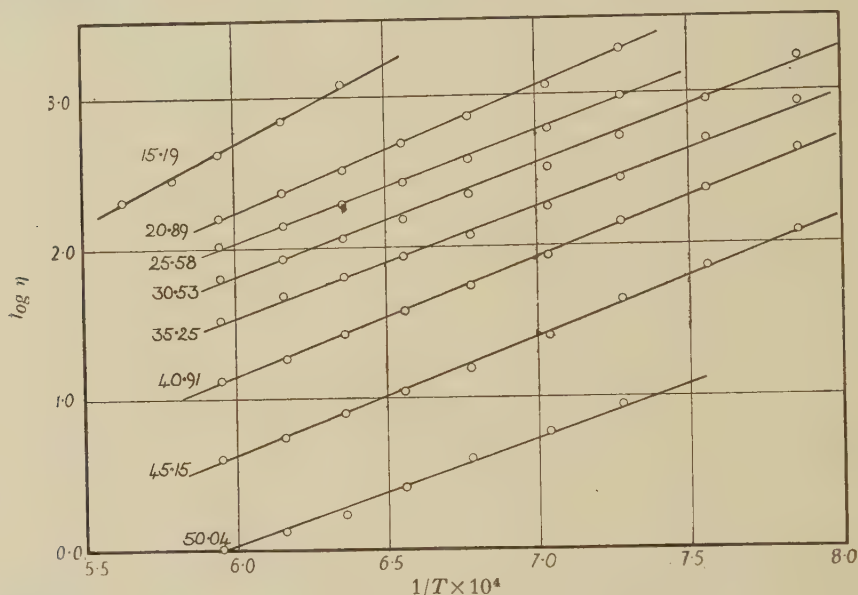
Figure 5. Relationship between viscosity and absolute temperature for soda-silica glasses at high temperatures. The different curves are denoted by their Na_2O contents.

the plot of $\log \eta$ against the inverse of the absolute temperature is linear within the accuracy of the experimental observations. This may be shown by plotting the results of Heidtkamp and Endell for the viscosities of the soda-silica glasses (E. Preston and E. Seddon, 1937), and is confirmed to a first approximation by figure 5, which shows the results of viscosity measurements at high temperatures for the same series of glasses made by the writer (1938).

E. Preston and W. E. S. Turner (1932, 1933, 1934 b, 1935 a, 1936 a) have studied the evaporation of the volatile constituents Na_2O, K_2O, Li_2O, PbO, As_2O_3 and SO_3 from molten glasses and have found the same laws obeyed as in room-temperature evaporations from normal liquids and solutions (E. Preston, 1933, 1935). In this connection it is well to note that the heats of evaporation

calculated for each constituent varied with range of composition, and since the energy required to evaporate one gram-molecule of a substance at a given temperature must be constant, it could only be deduced that chemical decomposition was first taking place in the solution, releasing the respective oxides. For a fuller discussion, the originals should be consulted (also E. Preston and W. E. S. Turner, 1934 a, 1935 b, 1936 b).

Electrical conductivity measurements have shown that the conduction of electricity is ionic and in no way different from the conduction of electricity through any metallic salt solution (E. Seddon, E. J. Tippett and W. E. S. Turner, 1932). Faraday's laws are obeyed and, indeed, hold good at lower temperatures when the glass is in its " unstable " condition and the processes of association or aggregation are proceeding rapidly with falling temperature. C. A. Kraus and E. H. Darby (1922) and C. A. Kraus (1922) made a quantitative study of the replacement of sodium ions by silver in a soda-lime-silica glass and obtained the following results, all the current being apparently carried by the sodium ions.

Table 2. Sodium-ion velocity and degree of ionization in a soda-lime-silica glass (Kraus and Darby)

Temp. °c.	Ion velocity cm./v./cm.	Ionization (per cent)
278	$4 \cdot 52 \times 10^{-8}$	76·5
295	$1 \cdot 46 \times 10^{-7}$	76·8
323	$3 \cdot 26 \times 10^{-7}$	77·05
343	$5 \cdot 9 \ \times 10^{-6}$	82·3

These workers concluded that ionization would be complete at temperatures around 1000° c., a temperature higher than the liquidus temperature of the composition investigated. It may be mentioned here that an empirical equation relating viscosity and electrical resistivity has been established for several glasses (C. L. Babcock, 1934 ; E. Preston and E. Seddon, 1937 ; K. Lark-Horovitz, 1934 ; J. T. Littleton and G. W. Morey, 1933) which is of the form

$$(\eta_1/\eta_2) = (r_1/r_2)^{\beta}.$$

β appears to be an index of the complexity of the glass, and is most probably related, among other things, to the degree of ionization of the " molecules " which provide the conducting ions. For simple soda-silica glasses, the value of β lies between 4 and 6, and this has been held to indicate that in viscous shear approximately 4 to 6 times as many bonds require to be broken as in electrical conduction through the same glasses (N. W. Taylor, 1939).

Work carried out in this Department by M. Manners and W. E. S. Turner (1940), and as yet unpublished, tends to show that the {surface tension, composition} relationships existing in the lithia-silica, soda-silica, and potash-silica series of glasses are precisely similar to those already known to occur in other solutions, such as, for example, aqueous solutions of $HgCl_2$ and KCl (G. Arcay and M. Marcot, 1930).

All these properties, including viscosity, lead to the view that at compositions corresponding to the occurrence of known chemical compounds a change in the {property, composition} curve takes place indicative of a change in internal constitution of the silicate solutions at these compositions. We may on this basis deduce the occurrence of configurational changes between the constituent atoms comprising a series of solutions, and it may be that changes of a similar type occur in the more usually encountered aqueous solutions of innumerable chemical compounds. X-ray investigations have, indeed, indicated these configurational changes in glass systems. In modern phraseology such changes of inter-atomic bonding appear to take the place of the older view of chemical compounds in solution. Although the most ready interpretation of such phenomena is in terms of these same compounds, associated and ionized to varying degrees, it seems that the chemist must revise a little his classical conception of these processes before he can reach agreement with the results of modern physical research which seeks for a more rigid interpretation, and, indeed, it has been stated that

> " The existence of certain compounds as the stable products of crystallization of a liquid is no evidence that they exist as such in the liquid, and no knowledge we have at present permits the identification of any compounds existing in the liquid state " (G. W. Morey, 1938).

§ 5. THE ATOMIC STRUCTURE OF GLASS

Whilst it cannot be denied that there is as yet more evidence to serve as a basis for the view that glasses are simply mutual solutions of the chemical compounds characterized by the respective equilibrium diagrams, associated or dissociated to varying degrees, this relatively simple chemical view is not in harmony with the interpretations placed on the results of x-ray investigations on glasses, which discredit such a conception. The x-ray measurements on glasses are at the moment probably more valuable as a contribution to the study of the liquid state than in the attainment of a satisfactory theory of the nature and constitution of glass, and in some respects the investigations appear to have out-stripped similar research which is vitally necessary on stable dilute solutions, for there can be little doubt that glasses are supercooled concentrated solutions, whatever the term " solution " be held to signify.

Since the initial investigations of P. Debye and P. Scherrer (1916), the results of researches too numerous to mention, and already summarized by J. T. Randall (1934), have been to show that in the liquid state there is a dynamic ever-fluctuating structure, any orderly array of atoms or molecules in the body of the liquid being only of a transient kind. The structures of relatively simple liquids such as argon, nitrogen, oxygen (W. H. Keesom and J. De Smedt, 1922, 1923), carbon tetra-chloride (H. Menke, 1932) and water (J. D. Bernal and R. H. Fowler, 1933) are comparatively well known, but the same cannot be said of the simplest solution.

The x-ray diffraction patterns of glasses are precisely similar to those of

normal liquids, broad diffraction bands being obtained, and the application of Fourier analysis to the intensity curves obtained has permitted the calculation of neighbour atom distances and the numbers of neighbours surrounding a given atom. In the case of the glass obtained by fusing silica, the structure
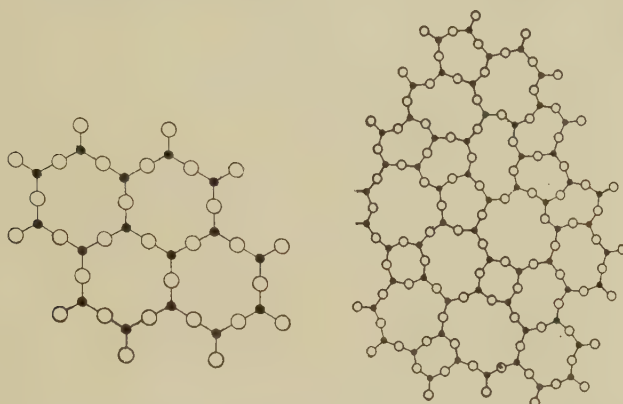
Figure 6. Left: Atomic structure of crystalline silica. Right: Structure of silica glass (after Zachariasen). Silicon atoms are denoted by black circles, oxygen by open circles.
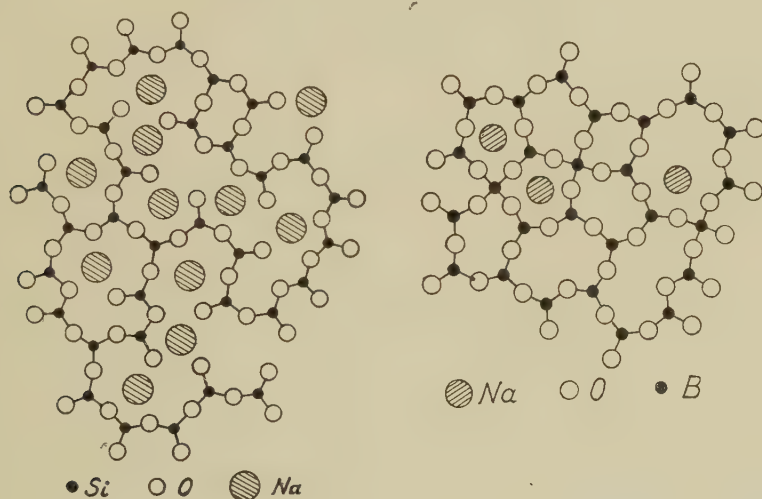
Figure 7. Two-dimensional representation of the atomic structure of a soda-silica glass (after Warren).

Figure 8. Two-dimensional representation of the atomic structure of a soda-boric-oxide glass of low soda content (after Warren).

deduced has much in common with that of silica in its crystalline state. W. H. Zachariasen (1932) regarded vitreous silica as a three-dimensional network in which each silicon atom was surrounded by four oxygen atoms spaced tetrahedrally, as in crystalline silica, at a distance of 1·62 A., the distinguishing feature being that the network lacked periodicity, no two atoms being exactly structurally

equivalent, due to the random orientation of each tetrahedral unit. Such a random network structure was confirmed by B. E. Warren (1934), and is shown, in two dimensions only, in figure 6. For the series of soda-silica glasses, B. E. Warren and J. Biscoe (1938) found a similar non-repeating network of Si–O tetrahedra with the sodium atoms occupying positions in the network adjacent to oxygen atoms bound only to one silicon atom instead of to two as in the normal Si–O lattice. The number of singly bonded oxygen atoms depended on the Na_2O content of the glass, each sodium being surrounded on the average by 4 to 6 oxygens as shown in figure 7.

For boric oxide glass, B. E. Warren, H. Krutter and O. Morningstar (1936) found a triangular co-ordination, each boron atom being surrounded by three oxygens and each oxygen being bound to two borons. Again the network lacked periodicity, and each BO_3 unit was randomly oriented with respect to neighbouring units as in the case of the SiO_4 unit in vitreous silica. For the soda-boric-oxide glasses, Warren and Biscoe (1938 b) found a structure analogous to that of the soda-silica glasses except that the boron atoms were partly in tetrahedral and partly in triangular co-ordination, the ratios of each type of bonding depending on the amount of Na_2O present in the glass. Such a structure is shown in figure 8, the sodium atoms occupying inter-lattice positions in the irregular non-repeating network. Maxima and minima in the physical properties of these glasses were explained in terms of the ability of the boron atom to exist in both types of co-ordination.

We may look upon such structures as a combination of order and disorder, and their further investigation along these lines may be most fruitful, as, for example, the consideration of immiscibility in liquid mixtures (B. E. Warren and A. G. Pincus, 1940).

§6. CONCLUSION

It is abundantly apparent that glasses at room temperatures, i.e., in their " solid " condition, possess the structure of the liquid state from which they were derived by supercooling. They have this advantage over normal liquids, which possess only an instantaneous structure, that their structure is static as in crystalline solids, and hence they may well be of great value in the further investigation of the liquid state. Particularly is this so with the one-component glasses such as SiO_2, B_2O_3, BeF_2 (B. E. Warren and C. F. Hill, 1934), As*(W. E. McCormick and W. P. Davey, 1935), and many organic compounds of which glucose is a striking example (G. S. Parks and W. A. Gilkey, 1929 ; G. S. Parks and J. D. Reagh, 1937 ; J. C. Lynmann and G. S. Parks, 1936).*

Ultimately there is little doubt that the constitution of glassy supercooled concentrated solutions will be shown to be in harmony with the constitution of the more customary solutions familiar to chemists and physicists.

* Organic glass-forming materials investigated by Parks and co-workers have included secondary butyl alcohol, dl-lactic acid, 3-methyl hexane and poly-isobutylene, entropy and free energy data being given for dl-lactic acid by G. S. Parks, S. B. Thomas and D. W. Light (1936).

§ 7. ACKNOWLEDGEMENTS

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A ROTATING DIFFERENTIAL PHOTO-ELECTRIC PHOTOMETER FOR PRECISION WORK

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ABSTRACT. Methods of photometry using selenium cells of the rectifier type are discussed.

The design of a new photometer in which two cells in opposition are rotated is given, together with an account of its performance. It enables a photometric study to be made of fluctuations of the order of one second ; also where photometric conditions are sufficiently stable the ratio of the candle powers of two sources of the same colour can be determined to well within one part in five hundred in a few seconds.

§ 1. INTRODUCTION

AN extended study of the candle power emitted by the crater of the carbon arc showed the importance of measuring the fluctuations with time in luminous output. The difficulty in measuring such fluctuations by means of visual photometry is too well known to require comment.

It therefore became desirable that an inexpensive photo-electric method of making such measurements should be devised. This paper gives an account of the development and use of a photometer of this kind. The value of such a photometer for measuring small and fairly rapid fluctuations can be illustrated by a study of the variation in candle power of a gas-filled lamp (Crompton 60 w.

120 v.) running on a perfectly constant supply. The two graphs (figure 1) show these variations: graph (*a*) with cap up, graph (*b*) with cap down. These results confirmed a suggestion made by one of us in 1928, which was that, in the construction of gas-filled photometric standards, if more care were taken to insure that the lines of flow of the gas should be reasonably smooth, a greater constancy of candle power would be obtained. When the cap is up (graph (*a*)) the fluctuations amount to $\frac{1}{2}$ % while with cap down (graph (*b*)) they are less than $\frac{1}{4}$ %. In
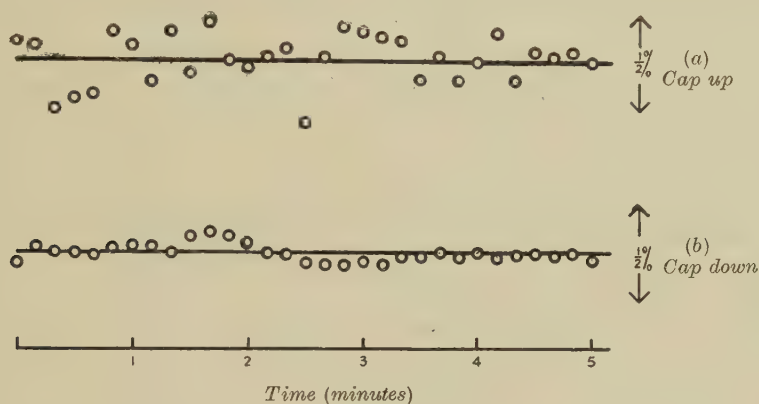
Figure 1.   Variations with time of candle power of a gas-filled lamp.

the first case, the hot gas meets irregular obstructions which necessarily cause turbulent flow, and as a result irregular cooling of the filament; in the second, the gases can flow unobstructed round the domed surface.

At first sight, the most obvious solution of measuring such fluctuations is to use a single photocell of the rectifier type, exposing it alternately to the unknown source and to a standard lamp. But on further consideration of the properties of single cells, the authors decided to develop a photometer using a differential method in an attempt to overcome the defects of a single cell.

§ 2. PROPERTIES OF CELLS AND THEIR EXPERIMENTAL ARRANGEMENTS

A single rectifier photocell is not perfectly adapted to direct-reading photometry. The properties of these cells are dealt with at some length by Preston (1936), Barnard (1939) and others. The following are their chief defects:—(1) The current response is never strictly linear, and the linearity is affected by a change in the resistance external to the cell. Deviations from the linear may amount to as much as 20 % when the illumination is changed from 100 to 40 foot-candles. (2) The response varies with temperature; a deviation up to 5 % may be expected for a change of temperature of 20° c. Furthermore, there is a hysteresis effect which makes readings depend on the past history of the cell. (3) The spectral response curve does not coincide with that of the eye. It agrees closely with that of the eye in the blue region of the spectrum, but in the red region it is much

too high.   The response may be 50 % of its maximum at 4000 A., where the sensitivity of the eye is zero.   (4) There is an initial drift effect which may last between 15 minutes and several days.   The history of the cell for at least 24 hours previous to use must be known.   The total drift may vary between zero and 10 %. Further, it has been shown by Elvegard, Lindroth and Larsson (1938) that this drift varies with the spectral quality of the light: the response may either increase or decrease with time.

Thus it is evident that when a rectifier cell is used as a direct-reading instrument, it is difficult to avoid an error of 1 % or even more.

There are several ways of overcoming the difficulties of using the single cell in precision photometry.

(1) *The rotation of a single photocell.*

This method has been used by C. H. W. Clark (1938) and by E. D. Wilson (1939).   The cell is rotated rapidly between the lamp under test and a substandard, and the commutated current from the cell is passed through a galvanometer of long period.   When the illumination on each side is the same, the current in the galvanometer will be an imperfect sine wave and the deflection of the galvanometer will be zero.   Wilson used a commutator having graphite sectors each of 120°; the brushes were also of graphite, since it was known (Baker, 1934) that the resistance for sliding graphite-graphite contacts was low and uniformly linear with current.   The cell was rotated at 1750 r.p.m. and a long-period galvanometer was used.

This method overcomes many of the difficulties in the use of a single cell, since uncertainties due to drift and temperature produce no effect on the result. It has the disadvantage, however, that either a galvanometer of long period has to be used or the cell must be rotated extremely rapidly.   In the former case it will not be possible to measure fairly rapid changes in candle power; while in the latter, the vibration may well become objectionable and there are likely to be spurious effects due to stray magnetic fields.   There may also be disturbing effects due to eddy currents in the pole pieces of the galvanometer if the coil is slightly out of centre.   An attempt has been made to eliminate these effects by injecting a direct current to oppose that of the photocell and commutating the resulting current.

(2) *The stationary differential cell*

Uljanin in 1888 hinted at the use of a differential cell when he constructed a cell consisting of a layer of selenium between two platinized glass plates.   He noted that with approximately equal illumination on the two sides the response was zero, but he does not seem to have used the cell for photometry.   Lange and Teichmann in 1930 described the use of two commercial cells placed back to back and used differentially for the comparison of light sources on an optical bench.   Gleason in 1932 used such an arrangement, obtaining equal response from the cells by placing strips of black paper over the stronger cell.   He was able

to compare lamps of the same colour to an accuracy of 0·1 %, and he obtained 0·5 % in heterochromatic work using filters.   L. A. Wood in 1934 discussed differential circuits on the assumption that the cell consists of a capacitance C shunted by a resistance R_p and in series with a resistance R_s.   If R_s is small compared with R_p, he deduced that a current-balancing circuit will have twice the sensitivity of a voltage-balancing circuit.   He also gave results of the use of the current-balancing circuit as a null reading method and as used for measuring out-of-balance illumination.

Unaware of the arrangements of these workers, one of us in 1937 suggested to Dr. J. W. T. Walsh of the Photometric division of the N.P.L. that a differential cell might be constructed consisting of two units formed one on either side of a single metal plate.   Dr. Walsh gave every assistance, and in consultation with Dr. G. P. Barnard it was decided that, although such an arrangement is the best from the thermal point of view, such a cell could not readily be made.   Dr. Barnard then constructed two separate cells having as nearly identical properties as
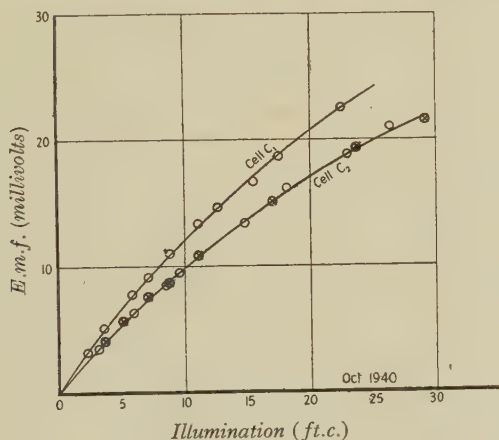
Figure 2.   Voltage response of Barnard cells.   In lower curve the points $\otimes$ show the response of cell C_1 when shunted with 10 000 ohms.

possible and had them tightly clamped back to back.   He writes that the aim was to construct two cells " to have equal responses for a given light source (i.e. the cells have the same absolute spectral sensitivity), and to have the same circuit characteristics (selenium resistance, barrier layer resistance, and platinum film resistance).   They were both made from the same selenium-sulphur molten mixture and were, in the course of manufacture, subjected to identical treatment. Of course, in view of the difficulties of manufacture, it is not possible to guarantee *ab initio* the cells to be precisely equal, but tests here at the N.P.L. showed that the differences were small.   Then again, the cells were so mounted back to back that in normal working (with no undue heating by a light source on one side only) the temperature gradient through the cells must indeed be very small ".

The cells were received in December 1937.   They were not quite equal in voltage response.   Cell C_1 had the greater output, as shown in figure 2.   In order

to equalize the voltages of the two cells, C_1 was shunted by a resistance which has slowly been increased since the cells have been in use. The graph shows the state of the cells in October 1940; it is seen that, when cell C_1 is shunted with 10 000 ohms, the voltage is almost exactly that of C_2. The value of the shunt at different dates is given below :—

Date	Resistance (ohms)		Date	Resistance (ohms)
Dec. 1937	1 100		Oct. 1940	10 000
Feb. 1938	2 500		May 1941	5 800 *
Jan. 1940	7 000			

The cells were used to compare the candle power of lamps. Provided that 15 to 20 minutes were allowed to elapse before readings were taken, satisfactory comparisons could be made. The drifts of the two cells are given in figure 3; it is seen that after 20 minutes the responses are sensibly the same.
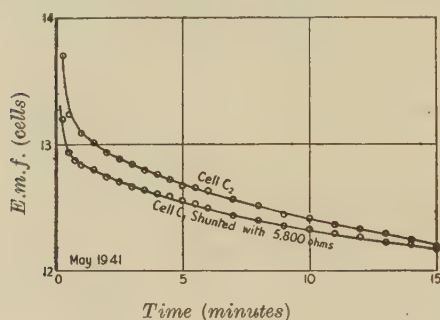
Figure 3. Initial drift of cells.
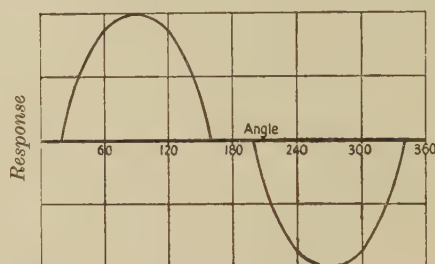
Figure 4. Wave form of single rotating cell.

Much work was done to find the most suitable electrical circuit. Experiments were made using a differential galvanometer, one coil being connected to each cell. Such an arrangement, which is a current balance, was more sensitive than the voltage balance (i.e. the coils connected in series with the two cells in opposition): but as a more suitable galvanometer could be obtained having a single coil, there was no advantage in pursuing the differential-galvanometer method. The resistance of the cells in opposition varies with the illumination.

Resistance (ohms)	1600	1800	2000	2200	2400	2600
Illumination (ft.c.)	18·5	12·5	8·3	5·7	4·2	2·7

For example, say the photometer head had an illumination of 12·5 ft.c. on both sides, then if both sources were extinguished for a short period the resistance would leap from 1800 ohms to nearly double that value.

(3) The rotating differential cell

An advance on the rotation of a single cell is the rotation of a differential pair, which again necessitates the use of a commutator. With a single cell exposed alternately to equal illuminations, the current has a wave form similar to figure 4.

* This low value is attributed to the fact that the two units had to be taken apart and could not be replaced in exactly the same relative positions.

So long as the cell rotates completely in a small fraction of the period of the galvanometer, there will be no deflection, since the wave form is symmetrical. In the case of the rotated differential pair, the current commutated is due only to the difference of voltage of the two cells. If the cells were identical, and the two sides of the photometer head were equally illuminated, then both A.C. and D.C. components would be zero. If the cells are not exactly equal, there will be a small A.C. component corresponding in amplitude to the difference of voltage
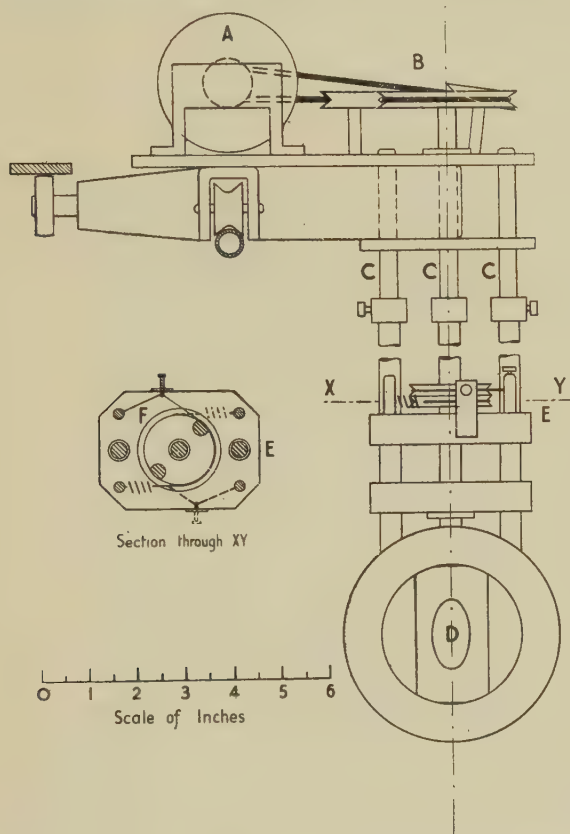
Figure 5. Construction of the photometer.

of the cells; but the D.C. component will again be zero. Such a system can be rotated as slowly as 100 r.p.m. using a galvanometer of 2-sec. period before there is any objectionable flickering of the galvanometer indicator.

It will be clear that such an arrangement not only overcomes troubles due to temperature differences, drift, and change of drift due to colour difference; but in this case there is no necessity to have a rapidly rotating cell unit and, furthermore, the sensitive galvanometer, which indicates the zero point, operates more nearly under normal conditions without having relatively large alternating currents passing through it.

§3. DESIGN OF THE PHOTOMETER

A photometer head fulfilling the conditions of the last section has been constructed, and has been in use for several months, during which it has given satisfactory service.   It has been designed for use on the optical bench in the Electrical Engineering Department at Queen Mary College; a description of the bench has been given in *A Symposium on Illumination*, p. 123.   The carriage has three wheels, two running on a guide rail and a third beneath a supporting rail.   The aim has been to secure a robust instrument which is nevertheless not so heavy as to be cumbersome.   The general design is shown in figure 5.
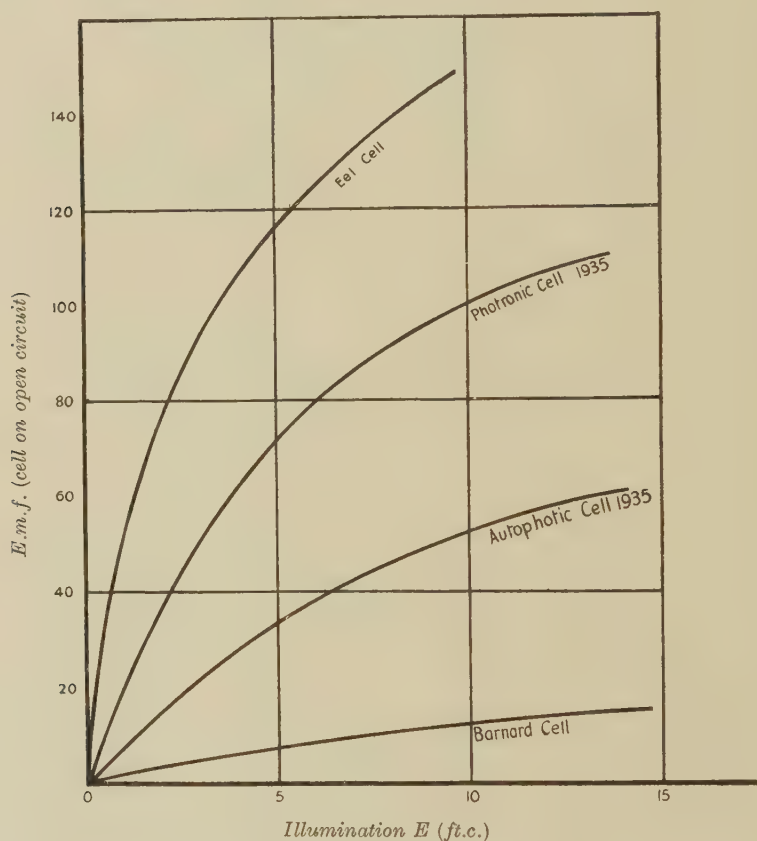
Figure 6.   Voltage response of various makes of selenium cell.

The photometer had to be made in the main of standard parts, consequently pulleys (B) had to be used to give a four-to-one reduction to reduce the shaft speed of a 240 v. 2000 r.p.m. motor (A).   Only 120 v. were required to drive the photometer shaft at 400 r.p.m.   The rods (C) were made to slide inside supporting tubes, thus giving a 2 in. vertical adjustment of the level of the head.   The centre shaft was earthed, thus providing a guard ring between the 240 v. D.C. mains and the sensitive galvanometer circuit.

The cells (D) used were those made by Dr. Barnard. These were retained on account of their stability and because they were well matched. As shown in figure 6, these are not so sensitive as other commercial cells which have been tested. The galvanometer used was a Tinsley type 4500 A. This has a resistance of 133 ohms, and while having a sensitivity of 540 mm. per microamp., has a period of only 2 seconds. Using this galvanometer, the photometer was sufficiently sensitive without using cells of greater output.

A special commutator (E) was designed so that any tendency for the brushes to be thrown off would be eliminated. The current is collected by flexible copper wires (F) passing round two pulleys, each of which has two contacts. Instead of being parallel, the wires were slightly splayed to prevent the galvanometer from being short-circuited. If this were allowed to take place, there would be
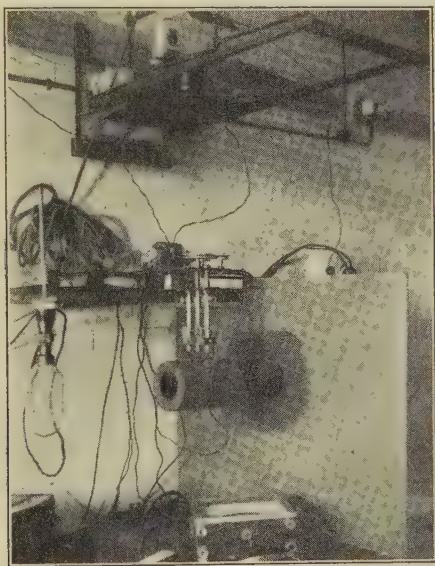
Figure 7. View of the experimental arrangement (near-side screen removed).

thermal currents from the junction of the collecting wire and the phosphor-bronze spring due to the heating arising from rotation.

It might be mentioned that a drop or two of medicinal paraffin oil was applied at intervals of a few days, when the photometer was in use, thus practically eliminating heating effects at the commutator.

Experiments were made to find the most suitable speed for the cells. The lower limit is set by the matching of the cells. When the cells were matched as accurately as possible by a shunting resistance across C_1, they could be rotated at a speed as low as 300 r.p.m. with only 1 mm. flicker of the galvanometer spot. Such a low speed was desirable not only for the comfort of the observer, but also because higher speeds must cause more heat at the commutator, with consequent possibility of thermal effects.

§ 4. PERFORMANCE OF THE PHOTOMETER

In order to test the precision which might be expected of measurements made with the photometer, the accuracy with which vacuum lamps could be compared was investigated. Two pairs of lamps were used : (1) bayonet-socket lamps having filaments all in one plane, (2) screw-socket lamps of the squirrel-cage type. The lamps were run in parallel at 100 v. as indicated by a potentiometer, and were placed so as to yield an illumination of 10 ft.c. at the photometer head. Five sets each of ten readings were made; after each set one lamp was removed from its socket and then replaced. Normal voltage having been restored, 5 minutes were allowed before further readings were taken. The maximum divergence from the mean of each set was 0·1 % in candle power, and the average
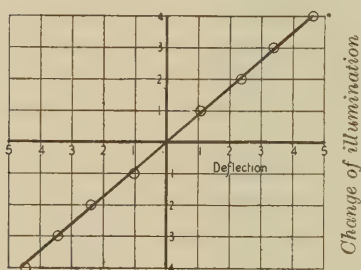
Figure 8.   Relation of galvanometer deflection to change of illumination.
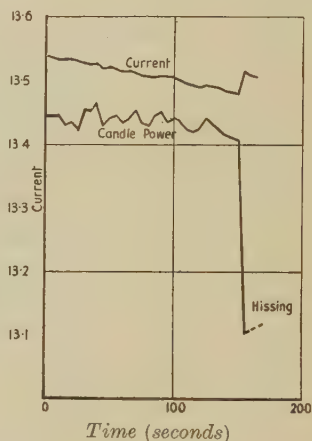
Figure 9.   Relation of candle power and current for carbon arc (graphite positive).

deviation of any setting from the mean was 0·06 % in candle power. This compares favourably with the 0·3 % for a Lummer-Brodhun contrast head given by Richtmeyer and Crittenden (1920). Judging from the consistency of a number of consecutive readings, if a single reading were taken, the value of the candle power obtained would be correct to 1 part in 1000. When, however, the means of each set were compared it was found that in the case of the bayonet-socket lamp with plane filament the means agreed only to 1 part in 250. This is probably due to the imperfect contacts causing change of current. In the case of the screw-socket lamp with squirrel-cage filament the means agreed only to 1 part in 150. The current in this case could be repeated, but it was extremely difficult to align the lamps so that they were facing in exactly the same direction, and the variations are most probably due to that cause.

The photometer may be used as a direct-reading instrument over a short range. Figure 8 shows the deflection of the galvanometer for a given change of illumination, and it is seen to be sensibly linear.

Where changes are taking place quickly, it is useful to adopt this method to find variations about a mean value.

As an example of the use of the photometer when one source is fluctuating, figure 9 is given. It shows how the candle power of a carbon arc, the positive of which is a graphite electrode, varies with the current passing through it. The arc was started with the electrodes close together, and left to itself so that its length steadily increased. The candle power and current both fell until hissing started; at this juncture the current rose and the candle power fell very rapidly. The readings were taken every 5 seconds, but it is evident that with photographic recording continuous records of the candle power of fluctuating sources could be obtained.

§5. CONCLUSIONS

In conclusion, it is claimed that a comparatively inexpensive photometer has been developed which will, in homochromatic photometry, give results with a self-consistency of four or five times that obtained by visual methods. This precision may be obtained by one observer and with much greater rapidity than can be obtained by visual methods. Further, an operator can take many more readings in a day without deterioration of results due to personal strain.

If the photometer is used in heterochromatic work, then either the sources must be matched in their spectra by the use of calibrated filters, or troughs containing solutions to correct the responses of the cells must be mounted on either side of the photometer. By the use of solutions of copper sulphate and of potassium dichromate, the selenium cell can be matched in response to the C.I.E. eye, and heterochromatic work may be carried out on a consistent basis.

§6. ACKNOWLEDGEMENTS

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THE PRODUCTION, PROPERTIES AND APPLICATIONS TO MICROANALYSIS OF ARCS POSSESSING LARGE-AREA ANODE SPOTS

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ABSTRACT.   Factors influencing the area of hot spots are briefly discussed.   Experiments are described in which an arc is struck in air at atmospheric pressure between a graphite cathode and a graphite anode—in the form of a cup at the end of a thin pillar. The cup is filled with powdered graphite which has been impregnated with a small amount of one of several suitable alkali and alkaline earth salts.   At first a localized spot appears at each electrode, but after a short time t_s the anode spot rapidly extends until it covers the surface of the powder.   This new and stable condition is maintained for a period t_b usually $> t_s$, until the supply of salt becomes exhausted (wholly by evaporation through the arc under suitable conditions), when the anodic spot again becomes localized.   The anode cup is then usually at a temperature between 800° and 2000° c.

t_s and t_b depend on the amount and nature of the salt, on the anode dimensions and on the arc current.   The relation between t_s and t_b and the other variables has been studied experimentally.   Results are shown graphically and a theory to account for some of these and other observations is proposed.

Conditions permitting a satisfactory general spectrographic system of quantitative

* Experimental work done at Imperial College, London.

microchemical analysis for mineral matter are discussed in the light of recently acquired knowledge of the arc and the new observations. A new method of analysis is suggested. Reasons for believing that the necessary conditions could be satisfied are given. Results obtained with a crude (and for rough work useful) approximation to this method are satisfactory. The limiting sensitivity for silver is in the neighbourhood of 10^{-9} gm.

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§ 1. INTRODUCTION

THE object of this investigation was to devise a satisfactory general system of microchemical analysis.

It is believed that the positive column of a low-tension arc in air at normal pressure (e.g. between graphite or metallic electrodes) represents, approximately, a state in which there is thermal equilibrium between electrons and gas particles (Compton, 1923; Ornstein, Brinkman and Beunes, 1934). The gas temperature in the carbon arc is known to range from about 4000° to 7000° K. (depending rather sensitively on the presence of traces of easily ionizable matter), whereas the electrode temperature cannot much exceed 4000° K. Throughout the discharge space, the ionization and excitation appear to be almost entirely determined by the local temperature, except near the electrodes (and in the case of states of relatively high energy), where the effect of the more direct process of electron impact is appreciable (Ornstein and Brinkman, 1934).

As is well known, in the region unperturbed by the electrodes, the gas temperature reaches a rather flat maximum on the axis and falls off gradually towards the periphery of the column (Ornstein, 1932). Now the diameter of the column is evidently connected with the distribution of current density in a section normal to the axis, i.e. in a thermal type of arc discharge, with the radial temperature distribution; and the diameter should therefore tend to decrease with increase in the radial temperature gradient. Normally, in an arc between metallic or pure graphite electrodes, the discharge narrows near a pole and ends in a localized hot spot. This constriction appears to be due to the perturbing effect of the relatively cold electrode and evaporated material on the thermic mechanism, and in this region the discharge changes type somewhat: ionization by electron impact sets in to compensate for diminished thermal ionization. This complex case will not be discussed further.

Now if the composition of the discharge atmosphere is such that a purely thermal type of discharge can exist when the gas and electrode temperatures are approximately equal, and if no relatively cold gas issues from the electrode, neither the normal temperature distribution across the column nor the thermic mechanism of the discharge will be greatly perturbed, and the column can then pass to the electrode without change in shape or type. An increase in diameter might, however, occur near the electrode if this is at a sufficiently high uniform temperature, since the radial temperature gradient in the adjacent gas will then tend to decrease. This appears to have occurred in experiments described

below, in which the anode surface consisted of powdered graphite (a relatively
poor thermal conductor) and the discharge atmosphere was cooled by introducing
a trace of some easily ionized substance by diffusion through the powder. The
temperatures of anode surface and *adjacent* gas were probably near 4000° K.—
the boiling point (? sublimation temperature) of carbon at normal pressure.
Under conditions fully discussed later, the anode spot becomes unusually large
for low-current arcs (5 to 10 amp.).

A useful consequence of this is that the total rate of transfer of heat from hot
gas to electrode is greatly increased on account of the increase in the area of contact
and in spite of a possible decrease in the rate of transfer per unit area.

In practice, the electrode temperature can be kept up over an extended area
by decreasing conduction losses. With graphite this can be done in two ways—
firstly, by constricting the electrode, and secondly, by using powdered instead
of bulk graphite, or otherwise decreasing the thermal conductivity of the electrode
material as in the case of the " carbons " at one time extensively used in arc lamps.
These appear to be mainly of some light and relatively non-conducting form of
carbon of which the particles are bound together by a substance capable of
supplying an easily ionized gas.

When the heat losses are thus decreased, the spot area and column diameter
also depend markedly on the partial pressure of the easily ionized constituents
in the discharge atmosphere.

This brief survey would be incomplete without mentioning that (for arcs
described below) spectrograms show that there is an axial temperature gradient
in the gas near the anode, which, indeed, is required to account for the
considerable fraction of the total energy being transferred to the anode.
Assuming (as is implicitly done above) that the chemical composition of the
discharge is substantially constant. this suggests that. receding axially from the
anode, the ionization per unit volume increases. Omitting details. this seems
to supplement the reason given above for the increase in the diameter of the
column towards the anode. for, roughly. the total ionization over any section at
right angles to the axis should be constant, as the current through such a
section it always the same.

§2. PRODUCTION OF LOW-CURRENT ARCS WITH LARGE-AREA ANODE SPOTS

The electrodes used were made from half-inch cylindrical rods of commercial
pure graphite.* The cathode (figure 1) was cone-shaped at one end, and the
anode, which was in one piece, consisted of a cup at the end of a short pillar which

* This was about as pure as is obtainable in prepared form : it was obtained from the Morgan
Crucible Co., London, in the form of rods. It contained minute but spectroscopically detectable
amounts of Si, Ca, V, Ti, Mg, Fe, B, Cu, Na and Li. Of these, Ca, V, Ti, at least, were not uni-
formly distributed, but occurred sporadically in small specks (Swings, 1935). The amounts of the
alkali and alkaline earth impurities were less by a factor of 10^3 or 10^4 than the smallest amount
of these substances impregnated into the graphite by means discussed below, and must have had
a negligible effect on the striking- and burning-time curves.

passed into the main rod. Both types of pole were made almost automatically in a turret lathe with specially designed tools.

The arc, with a variable resistance in series, was run from 220 v. D.C. mains and the current and the total voltage across the poles could be measured. Currents from 5 to 25 amp. could be used, and maintained approximately constant by hand adjustment throughout an observation.

The spectrograph was a Hilger large quartz Littrow instrument. The arc image (unit magnification) was formed on the slit by a system of quartz-fluorite lenses (focal length 25 cm.) tolerably free from aberrations. When desired, the plate holder could be moved with uniform speed at right angles to the direction of dispersion by a clockwork driving arrangement; when using this, a short (1 mm.) slit diaphragm was employed. A continuous record of the spectrum emitted by any section of the arc could thus be obtained. In several experiments of this type, the displacement of the plate with time was observed in order to check the uniformity of speed and to locate the spectrum corresponding to the state of the arc at any specified time.
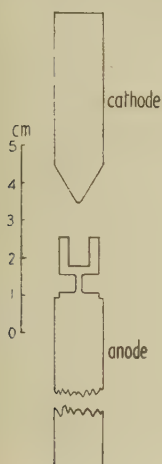
A known quantity of alkali (or other) salt was deposited from solution on to a known quantity of powdered graphite—initially of the same composition as the poles. Generally the deposition was effected under reduced pressure, though sometimes the mixture was dried in a copper oven. The former process was usually more satisfactory. The mixture was dried in a porcelain crucible if suitable, but occasionally copper or silica crucibles were used. It was then made as homogeneous as possible by stirring with a glass or silica rod or rubbing between filter papers, and placed in the anode cup and lightly pressed down with the rod to the level of the cup rim. With hygroscopic salts this process was carried out as rapidly as possible, and the electrode and contents were subsequently dried either under reduced pressure or in an oven. Usually several electrodes were thus prepared together.

A pair of electrodes was then placed in an arc-stand of the usual adjustable type, the cupped electrode being the anode and lower pole.

An arc having been struck between the cup rim and the conical cathode tip, which were then separated by about 1 cm., the following changes were observed (using dark viewing screens). For a few seconds extremely small hot spots were formed at the anode rim and the cathode. These moved about in the erratic manner characteristic of an arc between cold pure-graphite electrodes; the erratic motion is due to the specks of impurity. The anodic hot spot then passed on to the surface of the mixture in the cup, becoming more extended and stable and unaffected by any erratic motion of the *cathode* spot. The anode spot then moved slowly about over the surface of the mixture. As the anode became

Figure 1.

hotter, the spot seemed to maintain a constant area for some time, but later extended rapidly until, after a time (referred to as the " striking time ") which depended upon the dimensions of the anode, the current, and the amount and nature of the salt, it covered the whole surface of the powder. This condition, shown in plate 1 (*a*) (*b*) (*c*), was maintained for a time (the " burning time ") depending, but in a different way, on the same variables as the striking time.

When the salt at the surface of the powder becomes exhausted (as is shown by the sudden colour change of the arc), the anodic spot again becomes localized and unstable and anchors to the anode rim. Its area is then but slightly larger than it was immediately after the striking of the arc. In all the experiments the anode cup and contents were at this stage at a high temperature—between about 800 and 2000° c. (eye estimates)—depending c . previously mentioned variables Immediately after the reversion it was e dent, from the colour change of the anode cup, that the rate of transfer of heat from the arc had decreased considerably.

The surface temperature of the powdered graphite during the burning period could not be estimated accurately, but it apparently remained constant and much above the maximum temperature of the cup. From a rough comparison of the colour with that of a tungsten filament near its melting point, it was estimated to be about 3600° c.

The chlorides of Li, Na, K, Ca, Sr and Ba, and sodium silicate have been used successfully as impregnating agents for producing the extended spot.

§ 3. EXPERIMENTAL RESULTS

The curves in figures 2, 3 and 4 (p. 608) show the relations between directly observed quantities. Tables are omitted for reasons of economy.

Constants:

Internal diameter of anode cup 5·75 mm.
,, depth ,, ,, ,, 7.50 ,,
External ,, ,, ,, ,, 9·40 ,,
Length of pillar 4·73 ,,
Mass of normal charge of powdered graphite 0·09 gm.

Solution strengths:

Standard solution of $NaCl = 10$ gm. NaCl per litre of distilled water.
Standard solutions of $CaCl_2$, $SrCl_2$ and $BaCl_2$ contain respectively per litre amounts of Ca, Sr and Ba chemically equivalent to the Na contained in 10 gm. NaCl.
Sodium silicate solution contained 10 gm. Na per litre on the assumption that the formula was $Na_3Si_4O_9$.

Abbreviations:

t_s = Striking time (sec.). p = Pillar thickness (mm.).
t_b = Burning time (sec.). w = Wall thickness (mm.).
i = Arc current (amp.).

(a)   (b)   (c)
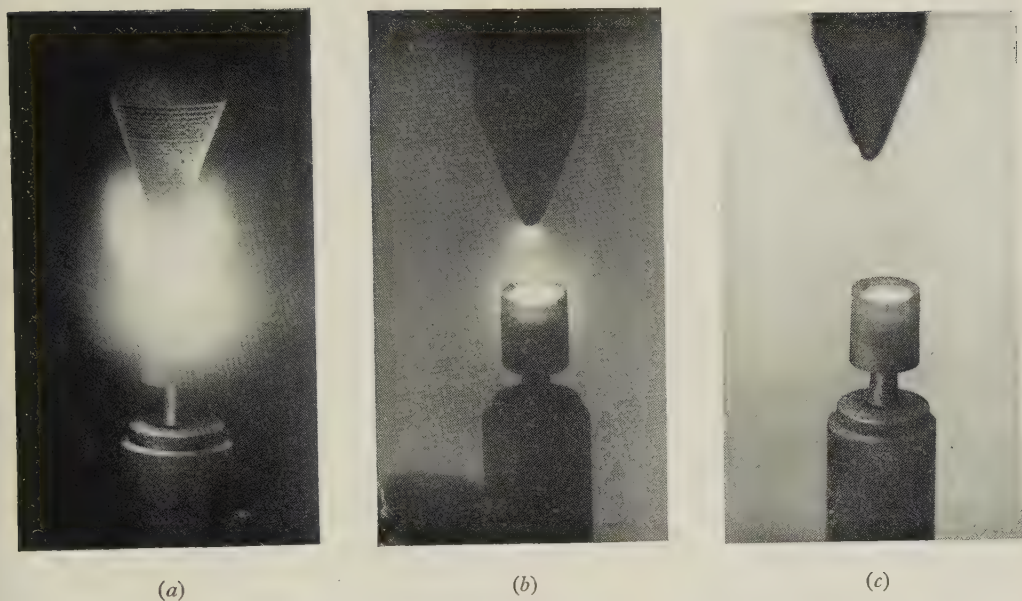
Plate 1. Extended anode spots using NaCl as impregnating agent.

(a) Photograph of the arc with filters suitable for showing the shape of the flame. Hot spot at anode just visible through the arc. Small electrode separation. Ring of light around the anode is due to halation and other defects in photographic recording.

(b) Filters suitable for showing the core of the arc, the anode spot (flame excluded) and the stable cathode spot obtained when the electrodes are close together, following a slight contamination of the cathode by condensation on it of salt evaporated from the anode.

(c) Filters exclude light from the core and flame and only the anode and cathode spots show. Large electrode separation with consequent relatively unstable cathode spot (no salt contamination) ; the cathode spot moved during the exposure and three positions are visible.
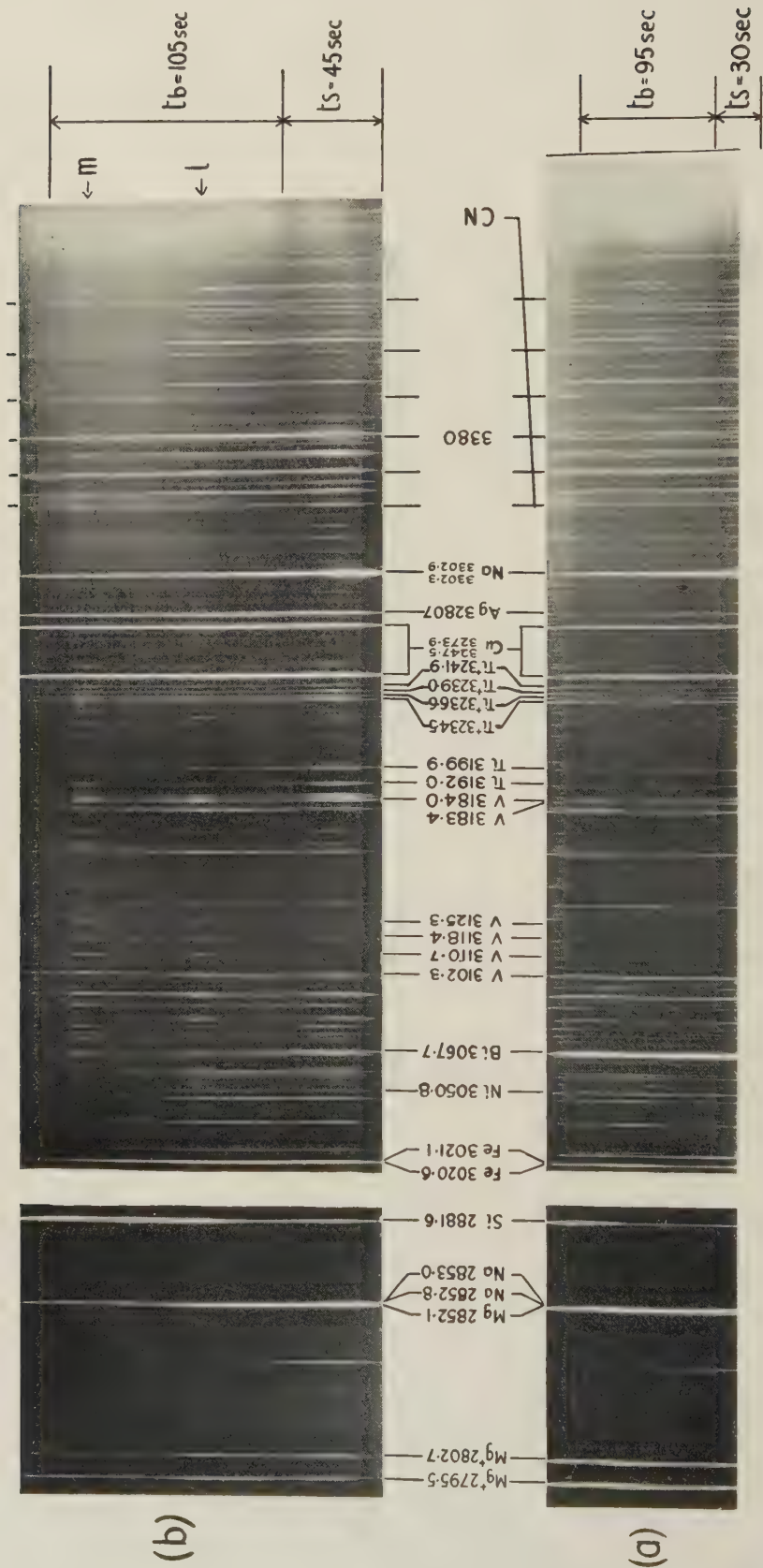
Plate 2. Moving-plate traces : (a) Sodium chloride as impregnating agent; (b) sodium silicate as impregnating agent.

Note. The first part of the (a) trace is not included because it is confused by a heavily over-exposed Fe arc spectrum.

q = Mass of impregnating salt per charge of graphite (gm.).

q_s = Volume of standard solution of impregnating agent per charge of graphite (c.c.).

g = Mass of charge of graphite (gm.).

$\bar{g}$ = Mass of normal charge of graphite (gm.).

§ 4. SPECTROSCOPIC OBSERVATIONS ON THE EVOLUTION OF THE ARCS

In several cases during the determination of the striking and burning times, the spectrum emitted by the arc was examined by means of the moving-plate spectrograph described above. In all such cases the image of the centre of the arc immediately above the anode was focused on the spectrograph slit. During the striking period it was necessary to move the arc-stand slightly, in accordance with the motion of the spot, in order to maintain the above condition; thereafter the arc-stand was stationary.

The records obtained show certain variations. Plate 2 (*a*) is an example of one type: NaCl (0·005 gm.) was used as impregnating agent. (Lines due to V, Ti arise on account of the association of these elements with the graphite; 10^{-4} gm. of Bi and 10^{-5} gm. of Ni, as subnitrate and chloride respectively, and traces of other elements were present; Mg, Fe and Si are prominent on account of the preliminary treatment of the specimens in a porcelain crucible.) Important characteristics of this type are: firstly, that the CN bands and the Na lines (in general, any arc lines due to the particular impregnating agent employed) remain at fairly constant intensity during the burning period; secondly, the ratio of intensities of an arc and a spark line of the same element remains almost constant during the burning period. Examples are 2852·1, 2795·5 A. Mg. I and Mg II, 3192·0, 3241·9 A. Ti I and Ti II, and 3199·9, 3239·0 A. Ti I and Ti II, respectively. Usually a different intensity ratio is apparent in such pairs during the striking period, when arc lines, in general, tend to appear more and spark lines less strongly than in the burning period. Several other plates qualitatively confirm the possibility of maintaining this constancy in the ratio of the intensity of arc and spark lines during the burning period. Unfortunately, the conditions necessary to produce it at will have not yet been experimentally determined, owing to the incompleteness of the observations with the moving-plate spectrograph.

For plate 2 (*b*), illustrating a second type, sodium silicate was used as the impregnating agent; in most respects it is a typical trace. Small quantities of several other mineral salts were included, viz., 2×10^{-6} gm. of Bi, Ni, Fe and Ag and 2×10^{-5} gm. As. The 0·5 c.c. of silicate used contained 0·005 gm. Na and about 0·008 gm. Si. In this commonly observed case the intensity ratio of arc and spark lines of an element does not remain constant during the burning period. There is a more marked variation during the burning period in the intensity of lines due to the impregnating agent (Na 2853 A. and Si 2881 A. in particular), and the intensity of the CN bands also varies more than in the first example.

The more refractory the mineral, the more retarded is the appearance of its spectrum at a given intensity during the burning period (cf. the behaviour of Si, Ag and Bi lines). During the striking period this relation is not noticeable.

The significance of the above observations is discussed in §§ 5, 6 and 7.

In order to ascertain whether the elements added to the charge used for plate 2 (*b*) had been completely distilled from the anode and not merely partly distilled and partly redistributed, the charge was removed from the cup at the end of the exposure and impregnated with NaCl. The anode cup was ground up and the resulting powder also impregnated with NaCl. These new specimens were tested in new anodes. The spectra showed only the merest traces of Ag and Ni and no trace of As or Bi.

Tests were also made to ascertain whether any appreciable fraction of the added salts was left behind in the crucibles used in the preparation of the specimens. It turned out that only a minute fraction need be lost in this way, provided that the glaze (or the crucible itself) is not seriously attacked by the substances treated in it.

Note. There are indications from the calibration curves of the plate motion (together with a slight tilting of the lines out of the direction of motion), that the increase in the strength of the spectrum at *m* (r.h.s. plate 2 (*b*)) is due to a slight irregularity in the motion of the plate (owing to faulty teeth on the plate-holder rack). This may also be the case at *l*, but, particularly here, another explanation is possible. It may be due to the development of an intense momentary supplementary discharge from the arc core to some point on the anode rim which had been contaminated during the preparation of the specimen. It is difficult, with a substance as hygroscopic as sodium silicate, to avoid this, and for this and other reasons it is not recommended for general use in connection with microanalysis. The above points are mentioned because on cursory examination it might appear that the fluctuation is of the same nature as that encountered when a trace is taken of the spectrum of an arc between unimpregnated graphite electrodes, when effects due to the random specks of impurity are apparent. This it certainly is not, and, apart from the instances mentioned, the evolution of the spectrum is quite regular with the type of arc described here.

§ 5. INTERNAL PROCESSES AT THE ANODE

An attempt is made below to discuss the internal anode processes qualitatively, and subsequently (§ 6) to account quantitatively for certain curves and observations of §§ 3 and 4.

We must first note that graphite is a peculiar electrode material, for besides being a solid, refractory, electrically and thermally conducting medium, it is capable, when raised to the appropriate fusion temperature, of absorbing any of the impregnating salts listed in § 2. This implies that (in the experiments described) the liquid salt could diffuse through the graphite, whether in bulk or powder form, at this temperature. At still higher temperatures, the vapour of the impregnating agent (or its dissociation products) could diffuse through the powdered graphite, no doubt much more readily than through the same thickness of the bulk material at the same temperature.

We picture the state of affairs inside the anode shortly after striking the arc as follows: In figure 5 (*a*), A represents the boundary of the anode spot; B, the

boundary of a layer above which the temperature is so high that the impregnating agent can exist in it only in the gaseous phase; below B, down to a layer C, we suppose that the impregnating salt is absorbed in the graphite in the liquid phase; below C, in the relatively cool region D, we imagine the salt to be in the solid phase and deposited on the graphite in very much the way that the mixture existed here before the arc was struck.

At the hot layer B, the liquid evaporates and diffuses, partly upwards (and subsequently partly into the arc) and partly downwards into D. The concentration of salt near A thereby becomes reduced and the arc takes a neighbouring path where a greater quantity of salt vapour can pass into the discharge. This process

Figure 5.

(a) Striking period. (b) Transition period. (c) Burning period.
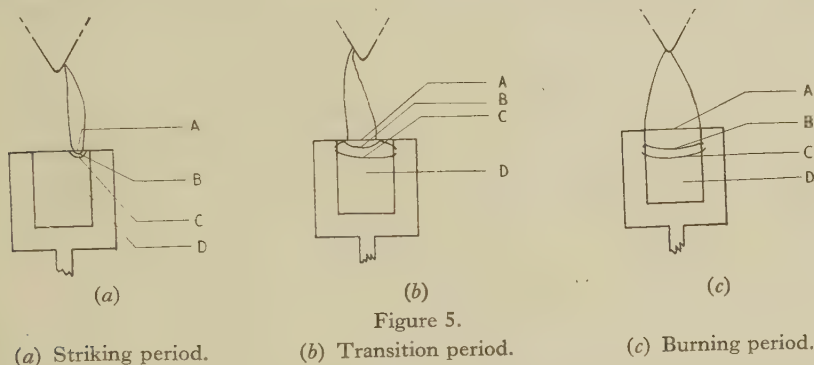
continues, and the spot moves about over the surface of the powdered graphite, seeking regions of greatest surface concentration of salt. By these means the concentration of salt at and in the region immediately below the whole of the exposed surface of the powdered graphite becomes much reduced, for the rate of diffusion of the liquid salt in the region B–C is quite small at the temperature now existing there. Just before the end of the striking period, we picture the state of affairs somewhat as illustrated in figure 5 (b). (It is to be noted that the " liquid " region B–C penetrates to some extent into the anode wall.) The salt concentration at the surface (whether as vapour at the spot or as solid or liquid elsewhere) is now fairly uniform and quite low, the spot by this time having completely traversed the surface. This matter is raised again in § 6.

It is reasonable to assume that up to this stage the rate of transfer of heat to the electrode has been almost constant, the losses being probably mainly by conduction down the pillar together with relatively small losses by radiation, convection and absorption of latent heat. The remainder of the heat produces the temperature distribution obtaining at this time.

At this stage, for reasons discussed in the introduction, the hot spot increases in area until it entirely covers the surface of the powdered graphite. Accordingly the surfaces A, B and C will become almost symmetrical about the axis of the anode (figure 5 (c)), as will also the related isothermal surfaces. The rate of

transfer of heat to the anode becomes much greater with the now fully extended spot.   We imagine that the region B–C (figure 5 (*c*)) moves towards the base of the cup, as a heavily damped wave of high temperature now begins to pass downwards. Simultaneously salt vapour diffuses upwards through the region A–B and so into the arc, and, as in the striking period, a portion distils downwards into the cooler regions.   In general, the rate at which salt vapour reaches the arc would not be expected to remain constant (it can be deduced from the moving-plate traces that the condition of fully extended spot does not necessarily imply a fixed concentration, for a given current, of the easily ionizable gas ; it can, in fact, persist over a limited range in the rate of distillation of this gas), but we should expect it to become increasingly more uniform *across the surface* with passage of time, on account of the increasing thickness of the layer of powder through which the vapour has to diffuse.   The cup now rapidly becomes hot enough to lose appreciable heat by radiation.

Conditions which determine the end of the burning period.   The burning period ends abruptly when the vapour pressure of the salt (more accurately, the vapour pressure of its easily ionizable dissociation products) falls below a certain very small critical value.   This state evidently arises when (*a*) the supply of salt in the cup has been reduced nearly to zero by distillation into the arc, or (*b*) when the rate of propagation of the high-temperature wave is inadequate to keep the vapour pressure of salt in the arc above the critical value.   A further, less important, case, (*c*), may arise, when the vapour pressure of the salt becomes greater over some part of the cup wall than over the powdered graphite ; this occurs when a high concentration of impregnating agent is used in thin-walled cups— e.g. when a charge of graphite is impregnated with more than about $0\cdot01$ gm. NaCl and *w* is less than about $0\cdot5$ mm.   In such a case, it is frequently observed that the spot oscillates several times between the powdered graphite surface and various parts of the top edge of the cup, until the salt vapour-pressure over the surface of the powder is reduced to the critical value, when the spot anchors permanently to the wall.   Apparently, with smaller amounts of NaCl or thicker walls, the salt diffuses into the walls too slowly for this to occur.   It will be observed that no attempt has been made to obtain the striking- and burning-time curves for $q>0\cdot01$ gm. (i.e. $q_s>1$ c.c.), although, no doubt, this could be done in certain cases.   With the possible exception of two or three observations recorded in this paper (low points on the t_b curves II, II in figure 2, p. 608), I do not think condition (*c*) determines the end of the burning period.   Oscillations were always looked for after the end of the first burning period, and, moreover (except possibly in the cases quoted above), the arc spectrum showed CN rather than the impregnating agent when the spot finally anchored to the wall.

The motion of the spot from powder to wall does not appreciably change the length of the discharge path. It is no doubt connected with a change in the sum of the resistances of the discharge and of the path through the anode cup.   The latter will be considerably less through the wall than through the powder.

$\{t_b, p\}$ *curve I* (figure 2, p. 608)

Condition (*b*) evidently determines the shape of this curve. Conduction losses, increasing with p, prevent the temperature propagation at a rate adequate to maintain the spot. If the salt distilled completely through the arc, t_b would increase with p, since the upward distillation would necessarily become slower with increase in pillar thickness. The operation of condition (*b*) requires that, at the end of the burning period, the region B–C must become closer to the powder surface for increasing values of p, other factors remaining constant.

$\{t_b, w\}$ *curves II, II* (figure 2, p. 608)

t_b increases at first rapidly with w and finally appears to approach a maximum. It should be possible to compute the form of this curve, assuming that t_b is the time required for the complete distillation of the salt. So far I have not been able to obtain a useful solution to the complex equations which approximately represent the state of affairs during the burning time. Since either condition (*a*) or (*b*) may determine the burning period, the precise significance of these curves is therefore doubtful. In either case we should expect the curve to droop at low w-values.

The mean temperature of the cup should rise more rapidly with thin walls than with thick, since the radiation (T^4) losses are proportional to ($r+w$), where r = the constant internal radius of the anode. Assuming that the salt distils from the anode completely in all cases (i.e. that the burning period is determined by condition (*a*)), we find a possible explanation for the droop in that the salt distils more rapidly than is necessary just to maintain the spot fully extended ; this is consequent in the lower radiation losses at a given temperature and therefore larger rate of temperature increase for low w-values.

On the other hand, the thermal conductivity of bulk graphite is greater than that of the powder; hence the wall thickness may play an important part in the propagation of the high-temperature wave. In this case, the effectiveness of the wall in aiding the downward propagation of temperature (and therefore the complete distillation of the salt) will decrease with decrease in w. Thus distillation of the salt may be incomplete at the low w-values: i.e. condition (*b*) may operate. Perhaps condition (*b*) determines the curve over the steep portion and condition (*a*) over the upper portion.

Finally, it is just possible that, with very thin walls, salt is lost during the burning period by processes other than distillation through the hot spot. These would probably arise not so much by diffusion of salt vapour through the walls as by diffusion of the liquid salt into the walls and subsequent evaporation into the atmosphere.

There is no direct evidence that this process occurs. In the experiments connected with the Sr curves V A, it was observed that a thin white film formed on the outside of the walls of some of the anodes which had been run at the highest currents. This was scraped off and tested qualitatively. No evidence of Sr was found ; the deposit apparently consisted of some V and Ti

compounds presumably left behind as a result of the appreciable combustion of the graphite occurring at the temperatures attained with these high currents. There is, however, good indirect evidence, from the possibility of condition (c) above, that this external evaporation process is possible at least for thin-walled anodes, particularly when q is large.

$\{t_b, i\}$ curves III A, IV A and V A (figures 3 and 4, p. 608)

There are three sets of curves, in which t_b is plotted against i for various con-centrations of several different impregnating agents. These bear a formal re-semblance, in spite of the somewhat different values of w in each set. An apparent exception occurs in the $CaCl_2$, $SrCl_2$, $BaCl_2$ group (curves V A in figure 4), where the curves droop at low i-values. This is doubtless due to the fact that, with these relatively refractory substances, the high-temperature wave is not propa-gated with sufficient velocity to ensure the complete distillation of the salt through the spot for low i-values. After the maximum has been attained, the shape of these curves resembles that of the other $\{t_b, i\}$ curves III A, IV A (figure 3) at low values of q_s. The fact that curves III A, IV A do not droop in the same way suggests that distillation is always complete here (or much more complete than in the case of the V A observations at low currents).

It is interesting to compare these curves, bearing in mind the melting and boiling points of the substances.

	CaCl$_2$	SrCl$_2$	BaCl$_2$	NaCl
M.P. (° c.)	772	873	962	801
B.P. (° c.)	1600	?	1560	1155

When these observations were made, it was believed that the burning period ended when the salt had completely disappeared from the anode, by evaporation through the hot spot alone or together with small losses through the walls. This belief was held because there was no tendency for the arc to re-strike to the powdered graphite surface after the burning period, and a CN spectrum was observed when the spot finally struck to the wall. It is just possible, however, that with low current and high q-values, an appreciable amount of salt may have remained near the base of the cup, especially near the pillar. If the observations are repeated, as seems desirable, this could be roughly tested by examining, powdered, a suitable part of the cup (or contents), testing in a new anode, and thus obtaining a measure of the amount of the salt directly from observations of t_s and t_b. This was attempted once or twice when thick-walled anodes had been used, but the amount of salt remaining was too small even to permit striking to the surface of the powder. However, this may not always have been the case, though I believe it was generally so on account of the very high final anode temperature attained with all but the lowest currents.

It would be interesting to repeat all the above observations, especially those with sodium chloride, using thicker-walled anodes (ca. 2 mm.), which should, I think, entirely prevent loss of salt by evaporation from the outside wall and, through the increased heat conduction to the base, ensure the complete passage of the salt into the arc.

§ 6. A FIRST-ORDER THEORY OF THE STRIKING TIMES

$\{t_s, i\}$ curves III, IV and V (figures 3 and 4, p. 608)

The following crude treatment seems to throw a good deal of light on the striking-time curves. Examination of the $\{t_s, p\}$ curve I in figure 2 shows that t_s is practically independent of p over a wide range. It seems very probable, then, that under the conditions of these experiments t_s is independent of the cup temperature. It is perhaps worth remarking that the rate of transfer of heat to the anode is quite small and that, except near the spot, the temperature of the anode never exceeds about 400° c. during the striking period and is, therefore, always well below the melting point of any of the impregnating agents for which curves are given. The area of the spot (for a given current) remains constant during the striking period until just before the commencement of the burning period, when, in a short time Δt_s, it increases quite rapidly. We shall neglect Δt_s and regard t_s as the duration of a steady state in which salt is being removed at uniform rate from a thin surface layer independently of the general anode temperature.

Assuming that the rate of transfer of heat to the anode is constant and equal to αi, we have, for the region *in the immediate vicinity* of the spot (roughly coinciding with A–B of figure 5 *a*):

$$\alpha i = X + Y, \qquad \dots\dots(1)$$

where X = rate of loss of heat by conduction
and Y = rate of absorption of heat by evaporation processes.
We shall assume that, essentially,

$$Y = L\frac{dq_e}{dt} = L\dot{q}_e, \qquad \dots\dots(2)$$

where L = the latent heat of vaporization of the impregnating agent, and $\dot{q}_e$ the rate of evaporation of the salt into the space above the spot. Let $\dot{q}_T$ be the (constant) total rate of removal of salt from the layer; a constant fraction, f, of this will distil downwards into the powdered graphite, where condensation will take place. We have then

$$f\dot{q}_T = \dot{q}_T - \dot{q}_e. \qquad \dots\dots(3)$$

Since the temperature of the spot is constant and is always very high in comparison with the temperature of the remainder of the anode during the striking period, we shall regard the conduction term X as being constant, to the approximation considered.

The conduction term includes the heat transfer by condensation, since over the region *outside* A–B (which with specified temperatures determines the magnitude of X) this heat is lost by conduction.

Combining (1), (2) and (3) we get

$$\alpha i = X + L\dot{q}_T(1-f). \qquad \dots\dots(4)$$

We assume that the thickness of the layer in which the concentration must be reduced to zero is, for any one salt, the constant fraction β of the depth of the powder. If q is the total amount of salt impregnated into the powder, then the striking time t_s is given by

$$\int_0^{t_s} \dot{q}_T dt = \beta q. \qquad \ldots \ldots (5)$$

Substituting (4), integrating (5) and rearranging, we get

$$t_s = L(1-f)\beta q/(\alpha i - X). \qquad \ldots \ldots (6)$$

If we now use Trouton's rule that $L = \lambda B$, where $\lambda = $ a constant and B the boiling point, we find

$$t_s = B q \lambda (1-f)\beta/(\alpha i - X). \qquad \ldots \ldots (7)$$

We thus find a satisfactory interpretation of the curves III (figure 3) in which $t_s(i - \text{const.})$ is approximately constant for a given q; for a given i, t_s is found to be roughly proportional to q, also in accord with (7). The same may be said (with somewhat less accuracy) of the curves IV (figure 3), but here the conditions probably differ somewhat because of the presence of silicon; plate 2 (*b*) suggests that the silicate decomposes in two stages. Finally, in view of the rather large experimental errors for the observations with alkaline earth chlorides (curves V, figure 4), it is perhaps not making too big a claim to regard these, taken individually, as consistent with (7). A detailed correlation of the three is yet to be made, but, qualitatively, the curves appear to have the expected mutual relation.

Note. The exact form of $\dot{q}_e$ for different impregnating agents is unknown, but it would accord with expectations if $\dot{q}_e$ increased with the ionization potentials of the easily ionized constituents of the mixture (so as always to keep the temperature and voltage across the arc low). This, incidentally, is consistent with what is expected with regard to the form of α; this should increase with the work function for an electron for the effective material of the anode. The work function increases from Ba to Ca. If we suppose, then, that $\dot{q}_e$ increases in the sequence Ba to Ca (i.e. with the ionization potential), then t_s, for $i = $ constant, should be least for Ca (the boiling-points of the different impregnating agents being nearly the same, in which case β and L should be constant). Such a trend shows up at low i-values, which, at any rate qualitatively, is consistent with what has been said. Without more experimental material it seems undesirable to go further into this.

Unfortunately it has not yet been possible to obtain a useful solution for the more important case of the burning time.

§7. A NEW METHOD OF MICROANALYSIS

The important practical problem of finding a general spectrographic system of quantitative micro-chemical analysis using the electric arc has received much attention but cannot be regarded as solved. An attempt is made below to indicate means by which it would now seem possible to overcome the difficulties whilst retaining the simplicity of the arc method.

It is required to estimate the amounts of the various mineral constituents of a given sample from the intensities of the corresponding atomic lines. With a suitable choice of conditions, which will be discussed later, the intensity of a line

is essentially a measure of the time integral of the intensity of radiation over the exposure period.

It is proposed to subject the unknown sample (termed the " primary " specimen) to a series of operations whereby a measure of this time integral for the most sensitive line of each element can be obtained. To evaluate the measures, the same series of operations will be applied to each of a number of calibration or " secondary " specimens containing known quantities of the elements in the primary specimen determined from a preliminary qualitative analysis. For convenience the relative abundance of the mineral elements in the secondary specimens should always be the same and roughly that of the primary specimen as estimated from the spectrum, and the specimens should form a graded series. The amount of any element m in the primary specimen will then be found by interpolation of the measure of integrated intensity of its most sensitive line (frequency ν_m) between the corresponding measures for the secondary specimens.

The operations proposed should provide a common scale of measurement for the amount of each element in any sample, irrespective of chemical form, if all the following conditions are satisfied :

(1) The whole of the metallic constituents of the sample are vaporized and subjected to the discharge.

(2) In a fixed region within the discharge, on the average every atom of a given element emits a quantum of radiation (frequency ν_m) the same number of times during the period of the operations on any particular sample.

(3) For each element, the radiation of frequency ν_m being photographed, from the region of the discharge in which (2) is satisfied, is always a constant fraction of the instantaneous *total* radiation.

(4) A measure of the time integral of intensity of the radiation photographed (from the above region) can be obtained for any frequency ν_m.

We shall suppose that the spectrum is excited in a short cylindrical region of low-tension arc-discharge in air at normal pressure * through which a gas is diffusing. The elements to be measured are assumed to be mixed with this gas in very small concentration. We make no assumptions concerning the distribution function over the region for any of these elements except that it never becomes very large in any place or at any time.

* This largely excludes considerations of band spectra. The core of the type of arc described here, like the ordinary low-tension arc (Jevons, 1932), is a poor source for the spectra of quasi-metallic molecules ; in fact, apart from the ever-present CN, and SiO bands (weakly developed with the sodium silicate impregnating agent), the only molecular spectra so far observed have been those usually attributed to the monoxides of Ca, Sr, and Ba, which, I believe, were weakly present in the core when the chlorides of these elements were used as impregnating agents.

However, even if the ground states of quasi-metallic molecules (e.g. oxide or nitride) were often stable at the temperatures encountered, it would not appear to affect the argument, and the only result would seem to be a decrease in sensitivity.

Condition (2) can be satisfied with this arrangement if:

(2.1) The excitation conditions remain constant over the region of the discharge. Since we appear to be dealing with a purely thermal type of arc discharge, this implies that the gas temperature (and composition) must remain constant over the region throughout the burning period. The abundant gas (of essentially constant composition) must therefore control the excitation: the distribution function referred to must never become large enough to affect this control.

(2.2) On the average the atoms of any particular element being determined remain in this region for the same period. If the period of the operations is always the same, they will do this if they diffuse across the section always with a characteristic speed for any element. Since we assume a constant gas temperature over the region (2.1) and an effectively constant composition of the gas, this speed will be governed by the rate of diffusion of the abundant gas through the section in addition to other factors assumed constant. There will be a characteristic speed for any atom m.

Let us now see how far these conditions could be realized in practice. For the arcs with fully extended anode spot already described, we have seen that:

(a) During the burning period the arc is quite stable so far as conditions at the anode are concerned.

(b) We can completely remove from the anode small amounts of fairly volatile " impurity " mineral salts impregnated together with the agent used for producing the extended spot. Under suitable conditions (including fairly thick anode walls) removal during the burning period is almost entirely by distillation through the arc.

(c) During the striking and burning periods the excitation conditions can be maintained fairly constant throughout each period, being appreciably less intense during the striking period. " Impurity " mineral salts, in amounts small compared with the amount of the agent used for producing the extended spot, do not appreciably affect these conditions.

(d) During the burning period the temperature of the exposed surface of the powdered graphite appears to be uniform.

Discussion of the conditions

(1) If the " impurity " mineral salts (now regarded as the constituents of the specimen to be analysed) distil through the arc only during the burning period, condition (1) could be satisfied. To ensure this it is suggested that the contents of the anode, of depth L, be built up in the following manner (see figure 6):—

A is a layer of powdered graphite (thickness x) impregnated with some agent for producing an extended spot. B (thickness d) contains the same concentration of this agent in powdered graphite which has also been impregnated with a suitable amount of the primary or secondary specimen. Finally comes a layer C, of the same mixture as A and of thickness $L-(d+x)=y$.
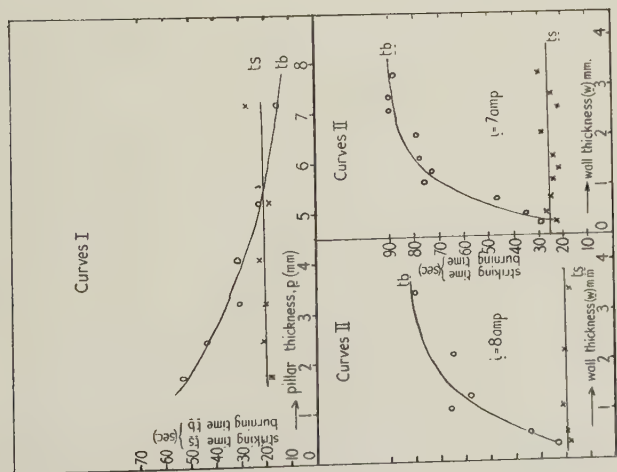
Figure 4.

Curves V: $\{t_s, i\}$ relations using $CaCl_2$, $SrCl_2$ and $BaCl_2$; $p=1.47$ mm., $w=1.10$ mm., $q_s=0.4$ c.c., $g=\bar{g}$.

Curves V A: $\{t_b, i\}$ relations corresponding to observations of curves V.

Curves VI A and B: $\{t_s, g\}$, $\{t_b, g\}$ relations for different degrees of tightness in the packing of the powdered graphite anode charge; $p=1.74$ mm., $w=0.62$ mm., q_s ($NaCl$) = 0.30 c.c.
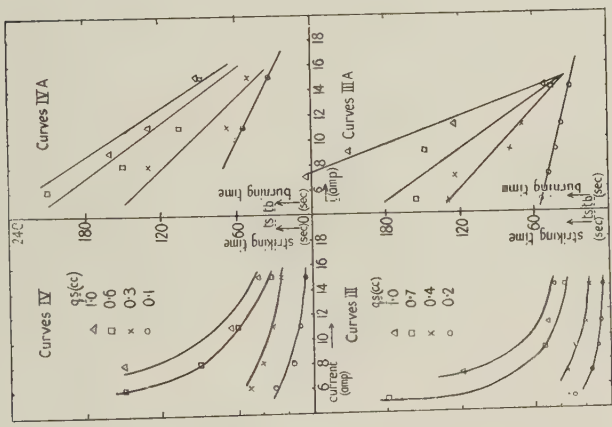

Figure 3.

Curves III: $\{t_s, i\}$ relations using $NaCl$ as impregnating agent; $p=1.74$ mm., $w=0.62$ mm., q_s ($NaCl$) = 0.2, 0.4, 0.7 and 1.0 c.c., $g=\bar{g}$.

Curves III A: $\{t_b, i\}$ relations corresponding to observations of curves III.

Curves IV: $\{t_s, i\}$ relations using sodium silicate as impregnating agent; $p=1.74$ mm., $w=0.62$ mm., q_s ($Na_2Si_4O_9$) = 0.1, 0.3, 0.6 and 1.0 c.c., $g=\bar{g}$.

Curves IV A: $\{t_b, i\}$ relations corresponding to observations of curves IV.

Figure 2.

Curves I: $\{t_s, p\}$, $\{t_b, p\}$ relations using $NaCl$ as impregnating agent; $i=8$ amp., $w=0.57$ mm., q_s ($NaCl$) = 0.30 c.c., $g=\bar{g}$.

Curves II: $\{t_s, w\}$, $\{t_b, w\}$ relations using $NaCl$ as impregnating agent; $i=8$ amp., $p=2.25$ mm., q_s ($NaCl$) = 0.30 c.c., $g=\bar{g}$.

Curves II: $\{t_s, w\}$, $\{t_b, w\}$ relations using $NaCl$ as impregnating agent; $i=7$ amp., $p=1.82$ mm., q_s ($NaCl$) = 0.30 c.c., $g=\bar{g}$.

Plate 3.   Amounts of added mineral elements (in units of 10^{-8} gm.).

Exposure		Ag	Ni	Bi
1	Primary specimen	65	50	82
2	Calibration specimen	3	3	3
3	,,	10	10	10
4	,,	30	30	30
5	,,	100	100	100
6	,,	300	300	300

Fe arc at base of diagram.

The value of y for the primary specimen could be chosen so that the substance being determined did not begin to distil until the fully extended spot had developed, and d should be such that the specimen completely distilled before the termination of the burning period—as would be possible when a sufficiently high anode temperature could be attained. Similarly for the secondary specimens, all of which should have the same values of d and x; but, in general, these would be different from those for the primary specimen (different compounds). These values of d and x would not be very critical (they could be determined for various classes of specimen by the moving-plate spectrograph) since we have only to ensure that the above conditions are satisfied. That being so, d should be as large as possible to avoid getting too much of the specimen into the arc at once, whereby errors due to self-reversal (discussed under (3)) would be increased and the excitation conditions might depart appreciably from the standard. For a very refractory specimen, small values of y and d are tolerable, whereas for a more easily vaporized substance y should be larger.

(2.1) Firstly, there is good evidence from plate 2 (*a*) (and others) that the average excitation conditions (i.e. the gas temperature) and gas composition can be kept constant in time across a diametral section of a *short* cylindrical region of the arc close to the anode surface. Although constancy of the intensity ratio of a given pair of arc and spark lines has not been verified by measurement, it nevertheless indicates approximately constant excitation conditions. Does the gas temperature remain tolerably constant across the element? Certainly the colour of the powdered graphite surface is uniform to a high degree during the burning period. If we interpret this fact as meaning that the temperature of the surface is constant, this receives a satisfactory explanation in that the graphite is undergoing a change of state (solid to gas). Hence very close to the surface the ordinarily rather flat temperature-distribution curve must be still further straightened out. We may assume for the moment that it is flat enough for our purpose (it is to be noted that, of all lines, the resonance lines would generally be least affected by a small variation in the excitation conditions).

(2.2) Let us confine attention to the motion of gas particles in the region under consideration. Here, and especially near the centre, turbulence caused by external convection will be a minimum (as follows from the geometry of the arrangement). Experiments indicate that this is not important in any case. Through this layer passes the gas from the anode, consisting of (*a*) CN (and possibly other carbon compounds) formed by chemical action primarily involving small particles of carbon projecting into the discharge.—Uniformity in the rate of formation of the carbon compounds will depend on uniformity in the temperature and chemical composition of the gas. It is probable that (except near an electrode from which rapid evaporation is taking place, e.g. near the localized cathode spot) the essential chemical composition of the discharge atmosphere remains fixed.—(*b*) the gaseous dissociation products of the impregnating agent, and (*c*) in very small proportion, those of the specimen undergoing determination.

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As already pointed out on p. 602, the rate of passage of (*b*) is probably constant across the region, and any disturbing effect of (*c*) is unimportant.

Hence (2.1) and (2.2) are resolved into the necessity of constancy in gas temperature across the surface. If this proves insufficiently uniform there would seem to be no difficulty about introducing a kind of guard-ring effect, whereby the constituents of the specimen distilled mainly through the centre of the arc, the radiation from the surrounding ring requiring merely a small correction.

(3) We could overcome the difficulty presented by condition (3) if, instead of projecting an axial section, the image of the arc was rotated through 90° and that portion of the arc immediately above the anode was condensed on the spectrograph slit (figure 7). With two qualifications we should then ensure that whatever might be the instantaneous distribution function of the excited matter in the space immediately above the anode, we should always obtain in the spectrograph a constant, and therefore representative, fraction of the total radiation over a solid angle of 4π from this region.
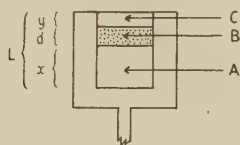

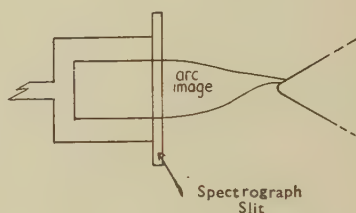Figure 6.   Figure 7.

The first qualification is of a geometrical nature, to the effect that only a narrow cone of light must enter the spectrograph, otherwise light is not abstracted from a thin flat circular zone, and any non-uniformity in the distribution (which might be important with a refractory specimen) will introduce errors. This qualification is almost automatically fulfilled with the type of spectrograph which would normally be used, with small aperture (and high dispersion), e.g. the Hilger-Littrow type. The condensing lenses should be well corrected for aberrations, particularly chromatism.

The second qualification is that the *raies ultimes*, which we must use for greatest sensitivity since these are usually the resonance lines, are subject to self-reversal, so that to some extent an internal redistribution of energy takes place. This effect can be made negligible with sufficiently small amounts of the elements. The amount of the primary specimen should therefore be just sufficient to give the *raies ultimes* with adequate strength for micro-photometry, although even with considerably larger concentrations the lines are almost free from self-reversal. By bringing about this state of affairs, the excitation conditions will not be appreciably disturbed by the presence of the vaporized specimen.

(4) There is no theoretical difficulty in satisfying condition (4). Failure of the photographic reciprocity law will probably not cause serious errors if a suitable choice and judicious use of photographic plates are made, so that the relation between the blackening and the product of intensity and exposure time

is roughly linear. The threshold exposure error for all frequencies might be greatly reduced by a suitably graduated pre-exposure of the plate.

It appears, then, that quantitative analysis is practicable if observations are confined to the burning period. A suitable procedure would be to take a micro-photometer trace *in the direction of the line* for a suitable line of each element. Any particular frequency would be traversed in a single run for all exposures—primary, secondary and " blank test ".* To obtain the amount of an element it would merely be necessary to interpolate the area under the micro-photometer trace for the chosen line for this element in the primary specimen exposure, between the corresponding areas for the same line in the calibration exposures.

The postulates made are not likely to be rigorously fulfilled in practice, but a number of adjustments are possible, and (perhaps with modifications) the scheme suggested here may well provide a basis for a more general, convenient, sensitive and accurate spectrographic method of micro-analysis than has hitherto been possible.

The following measurements, obtained by a crude approximation to the scheme outlined above, may be of interest.

An aqueous solution of known concentration containing salts of Ag, Ni and Bi was made up. Seven pairs of graphite poles with thin anode pillars and 2 mm.-thick anode walls were prepared. A charge of powdered graphite was placed in each of seven porcelain crucibles, and $0 \cdot 2$ c.c. of the standard solution of sodium silicate was added to each. To one of these was added 1 c.c. of the above Ag, Ni, Bi solution, and to five of the others were added 3×10^{-8}, 10^{-7}, 3×10^{-7}, 10^{-6} and 3×10^{-6} gm. respectively of each of Ni, of Bi and of Ag, added volumetrically from dilute standard solutions of salts of these metals prepared previously. The solution in each crucible was made up to the same amount with the distilled water used in preparing the standard solutions, which had been kept in a bottle of the same kind of glass as the standard solution bottles. The seventh crucible contained only graphite and silicate solution made up to the uniform volume with distilled water. This distilled water was manipulated by the same routine procedure as was used in the preparation of the other specimens.

The specimens were carefully dried in a copper oven, crushed and introduced into the anode as described in § 2. They were then arced (with the exception of the " blank "), using a current of 12 amp., and the spectra were photographed side by side on the same plate, from the beginning of the striking period to the end of the burning period. These times were almost exactly the same. The *axial* section of the arc just above the anode was condensed on the spectrograph slit, with occasional guidance during the striking period by means of the lens system already described. Unfortunately the " blank " specimen was damaged, but subsequent investigation showed that neither Ag, Ni nor Bi was liable to be

* A " blank test " specimen is a standard charge of graphite impregnated with the same amount of the agent for producing the extended spot as each of the other specimens. It is to serve as a check against spurious introduction, during the preparation of the specimen, of the elements being determined. The practical difficulties in excluding or allowing for such introduction are, in the writer's opinion, much over-rated ; with care there need be little difficulty.

inadvertently introduced, though Cu, presumably as oxide scales from the oven roof, was liable to be introduced in this way. Mg and Fe were introduced from the porcelain crucibles as shown by a further test in which silica vessels were used. As already stated, the vacuum-desiccation process is better than the oven method, especially when boiling under the reduced pressure is avoided.

Plate 3 shows the result of this series of exposures. It is at once evident that the limiting sensitivity for Ag is in the neighbourhood of $(5 \text{ to } 10) \times 10^{-9}$ gm. Similar tests with NaCl as impregnating agent gave a sensitivity about five times that obtained with the silicate. We can therefore conclude that the limiting sensitivity for Ag by this method is in the neighbourhood of 10^{-9} gm.

The amounts of Ag, Ni and Bi as estimated by visual interpolation are about $(3 \text{ to } 9) \times 10^{-7}$ gm. in each case. The actual concentrations were $Bi = 5 \times 10^{-7}$ gm., $Ag = 6 \cdot 5 \times 10^{-7}$ gm., $Ni = 8 \cdot 15 \times 10^{-7}$ gm.

In this test (which is only suggested for comparatively rough work on the more volatile specimens) we have not attempted to avoid, but merely to reduce, the above-discussed sources of error. The striking time was small compared with the burning time, so that most of the " impurity " elements distilled during the burning time. From previous experiments it was fairly certain that they would be almost completely removed from the anode, but not that the excitation conditions were constant during the burning period or that the rate of diffusion of the impurity elements was uniform over the surface. Except possibly with Bi, the distribution function would not remain constant during the burning period, so that with an *axial* section of the arc we are not extracting a representative fraction of the total radiation. Finally, the amounts of the elements used are much too large to take full advantage of the known properties of photographic plates. However, the test certainly reveals the sensitivity of the method.

It may perhaps be pointed out that this abnormal sensitivity may be due to the facts that (1) the whole of the specimen is used, (2) it distils through the arc relatively slowly so that each atom can emit many more times than if the distillation were rapid (in many cases it is almost explosive as, for instance, in the case of the spark), and (3) the excitation conditions in this type of arc are very efficient in exciting resonance lines in the wave-number region 15 to 40×10^3 cm.$^{-1}$.

Finally, the statement of Swings (1935) (l.c. p. 48) and others, to the effect that graphite electrodes should be avoided in analysis because of localized impurities, is invalid when the above method is used. The usual complaints are that the electrode spectra are not reproducible and that often the specimen being analysed appears to cause an increase in the strength of the pole impurity lines or even make it appear that the corresponding elements belong to the specimen when such may not be the case. This phenomenon arises when the specimen contains a substance which causes extension of the hot spot, though this fact does not appear to have been remarked hitherto. The increase in the intensity of the impurity lines in the presence of the specimen can be accounted for by the fact that more heat is transmitted to the electrode and the excitation conditions are altered. The greater heat transmission and the increase in area of the spot

average out the volatilization of impurity from a sporadic and often small superficial effect to a uniform and larger volume effect. It will be observed that this usually troublesome effect has been turned to good account in the method described above, in which the pole impurity spectrum is accurately reproducible (cf. plate 3, Ti$^+$ lines 3234·5 to 3242·0 A.).

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THE DEPENDENCE OF THE SECONDARY ELECTRONIC EMISSION PRODUCED BY GAMMA RADIATION UPON THE DIRECTION OF THE RADIATION

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ABSTRACT. Experiments are described which show that the electronic emission from a sheet of material, due to gamma radiation, depends upon the direction of the radiation with respect to the sheet. In certain directions, the emission from a sheet of material is equivalent to that from a sheet of " air-wall " material (graphite). An approximate explanation of these findings is given.

An examination of the electronic emission from bone, when it is irradiated with gamma radiation, indicates how the energy absorption per röntgen of gamma radiation may change at boundaries between bone and soft tissues.

§1. INTRODUCTION

THE problems connected with the emission of secondary electrons from matter when high-voltage radiation falls upon it have always taken a most prominent place in the physics of radiation therapy. The absorption of radiant energy within tissues and the measurement of this energy, the best primary

and secondary filters and many other problems, are all ultimately bound up with the question of secondary electronic emission. The experiments to be described in the article provide some further information concerning the secondary electrons generated by gamma radiation.

Data concerning the forward (emergence) and backward (incidence) electronic emission from matter when irradiated with gamma radiation have been available for some time and have been summarized and extended by Quimby, Marinelli and Blady (1939). Thus it is known that the emergence emission is a minimum for materials of intermediate atomic numbers, while the incidence emission increases continuously with the atomic number of the irradiated material. The present experiments were designed to obtain some idea of the emission at angles between these two limiting directions.

§ 2. APPARATUS AND METHODS

The essentials of the apparatus used are shown in figure 1. An ionization chamber C is designed so that one wall of it can be changed as required. The air volume of the chamber is a cylindrical cavity within a cylindrical piece of amberoid
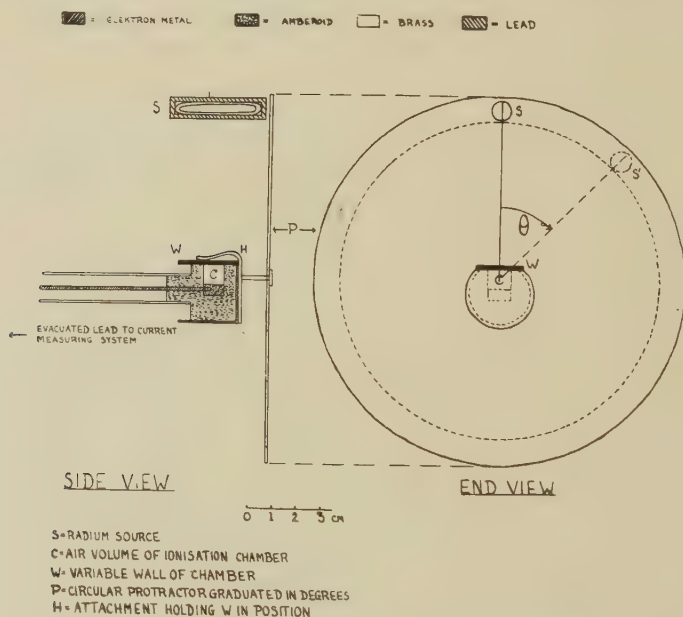
Figure 1. Design of the ionization chamber, arrangements for changing the wall material, and the position of the radium source.

which fits inside an earthed brass tube; the joint is waxed to render the tube airtight so that it may be evacuated. At the bottom of the ionization chamber is a tightly fitting disc of elektron metal which serves as the collecting electrode, and a lead from this passes down the evacuated tube to a current-measuring

apparatus. The latter was a variation of the usual Townsend balance method and has been described elsewhere (Wilson, 1937). The inner surface of the vertical walls of the chamber (of amberoid) are very carefully polished to render them highly insulating. The upper surface of the amberoid, on to which are fitted the different walls W, was very accurately worked so that the flat sheets of material fitted accurately to the surface to ensure that the air volume of the chamber is always the same. The wall W is raised to a potential sufficient to ensure saturation current under working conditions. Preliminary experiments showed that in order to obtain consistent results, free from the effects of static charge upon the outer surfaces of the amberoid, it is necessary to cover these surfaces with a conducting surface maintained at a constant potential. The amberoid was therefore fitted with a thin sheath of elektron metal such that it made contact with the wall W as indicated in figure 1. The walls W are held tightly in position by a light brass spring-attachment H fitted to the elektron-metal sheath, which also carries the celluloid protractor P. The presence of these fittings can hardly affect the ionization in the chamber, since the chamber walls were all at least as thick as the range of any secondary particles that might be produced, and any effects of scatter and absorption must be very small.

The radium source was 20 mgm. of radium element contained in a glass tube with walls approximately 2 mm. thick. This was contained within another cylinder of lead with walls 2 mm. thick. This filtration would correspond to an effective wave-length of gamma radiation of about 14 x.u. The source S is mounted relative to the ionization chamber as shown in figure 1, and can be moved round the protractor into any position S' as indicated. The position of the source relative to the chamber was designated by the angle θ between the vertical and the line joining the centres of the radium source and ionization chamber.

For all measurements of the ionization within the chamber for a specific set of conditions, readings were made for both positive and negative potentials applied to the wall W. The mean of these results, which differed by only a few per cent, gives a value from which any error due to ionization losses is eliminated.

A variety of elements and substances were used as materials for the wall W. The thicknesses of these walls were always such as to be at least equal to the maximum range of the secondary electrons generated in them by the gamma radiation. In some cases the thickness was greater than this critical thickness, but the excess was never so great as to introduce serious absorption factors. The possibility of this will be considered again later. Details of the wall materials which were used are given in table 1.

A comparative method was used to examine the electronic emissions from these various walls, the ionization obtained with any wall material in position being compared with that obtained when an " air-wall " material (graphite) is used. The ratio of the ionizations measured with these two sets of conditions serves as a measure of the electronic emission from the wall in question relative to that from an air-wall, since the emission from the rest of the chamber will be

the same in both cases. The excess of this ratio over unity is not, of course, a direct measure of the added emission due to the new wall as compared with that from the graphite wall, because the emission from the rest of the chamber

Table 1. Details of wall materials and their thickness

Wall material W	Atomic number Z	Thickness in mgm./cm.^{2}	Wall material W	Atomic number Z	Thickness in mgm./cm^2
Graphite	6	650	Silver	47	525
Elektron metal	13	700	Gold	79	966
Sulphur	16	768	Lead	82	966
Iron	26	589	Bone	?	760
Copper	29	536	Amberoid	?	606

is always included. The ratio does serve, however, to indicate the kind of variation of emission that occurs. Provided that, for individual comparative measurements, the radium source is kept at a fixed distance from the chamber, it is immaterial whether this distance is varied slightly for the different wall materials. In all the experiments the distance was fixed as nearly as possible at 7 cm.*

§ 3. EXPERIMENTS AND RESULTS·

(a) *The " emergence " and " incidence " emissions*

The first experiments covered familiar ground in an examination of the emergence and incidence electronic emissions for the various materials. In addition to conducting elements of definite atomic number, a non-conducting element, sulphur, was used, and also two other indefinite materials, namely, bone and amberoid. To render the walls of sulphur, bone and amberoid conducting, a grid of Indian-ink lines was drawn on the inner faces, while the outer faces were thickly painted with " Zebo " grate polish. The bone was a specimen of compact bone taken from a human femur.

The comparative readings were made for all the materials with the source vertically above the chamber ($\theta = 0°$), which gives the emergence emission, and also with the source vertically below the chamber ($\theta = 180°$), which gives the incidence emission. In the first case, corrections were applied for the absorption of gamma radiation in the materials of the upper wall; the effect of these corrections upon the ratios described above was only of the order of 1 or 2 per cent. Obviously no such corrections are necessary in the second case.

Figure 2 shows the results obtained in this manner, the full line showing the " emergence " emission and the broken line the " incidence " emission. The curves show the same general characteristics that have been found by others (Quimby *et al.*, 1939). It is, however, of interest to note that interpolation, in

* See note at end of paper concerning these matters.

both curves, of the values obtained for the bone and amberoid walls suggests that the effective atomic number of the bone is of the order of 12, while that of
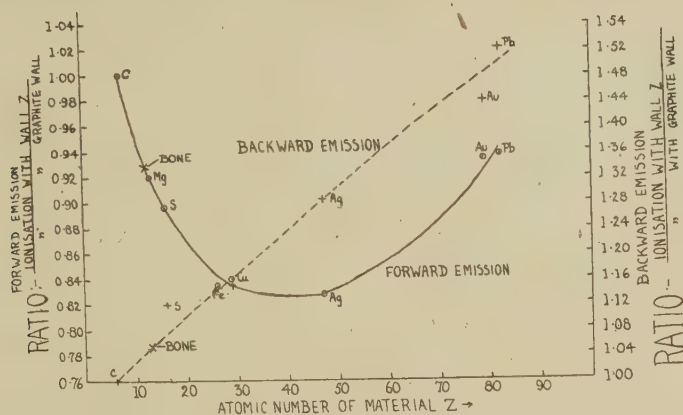

Figure 2. Relation between the atomic number and the measured ionizations for emergence and incidence emissions.
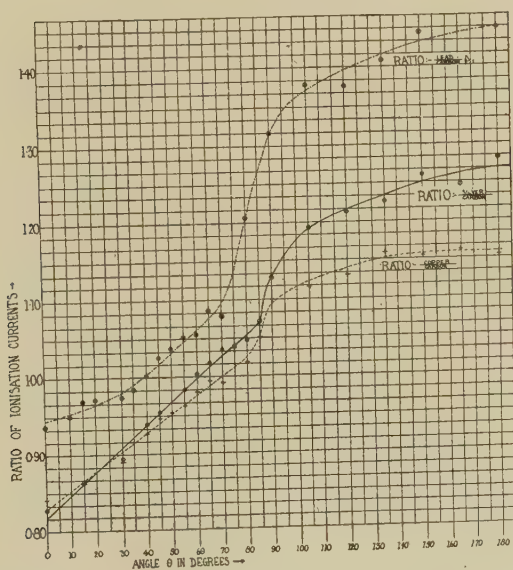

Figure 3. Ratios between the angle θ and the relative electronic emissions for walls of lead, silver and copper.

amberoid cannot be very different from that of graphite. Calculation of the effective atomic number of bone by the usual methods * gives a value between 15 and 16.

* The effective atomic number $\bar{Z}$ is obtained by means of the relation

$$\bar{Z}=[aZ_1{}^{2 \cdot 94}+bZ_2{}^{2 \cdot 94}+cZ_3{}^{2 \cdot 94}+ \ldots]^{1/2 \cdot 94},$$

where a, b, c, etc., are the fractional contents of electrons belonging to elements of atomic numbers Z_1, Z_2, Z_3, etc.

(b) *The dependence of electronic emission upon the angle θ*

In the next experiments, the electronic emissions from the lead, silver and copper walls (compared with that from graphite) were examined for a range of values of the angle θ between 0° and 180°. The ionization ratios thus obtained in the three cases are shown in figure 3, plotted against the angle θ. It is seen that as θ increases from 0° to 180° the emission from each of the walls, as compared with that from graphite, rises continuously but not regularly. The ratio rises from a value below unity to a value greater than unity. Thus, in each case, at
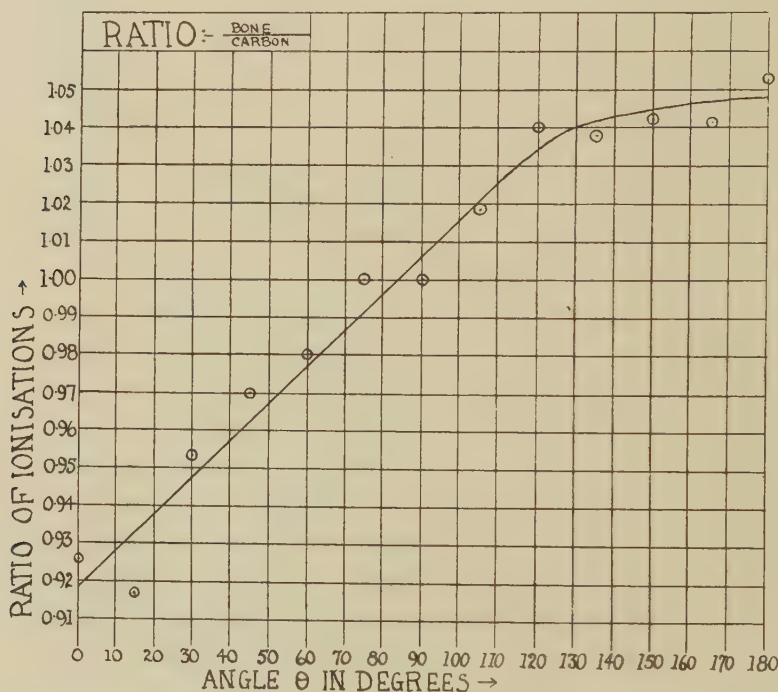

Figure 4. Relation between the angle θ and the relative electronic emission from bone.

some particular value of θ, where the ratio is unity, the emission from the wall is equivalent to that from the graphite wall.

Because of possible clinical interest, a similar experiment was carried out with the bone wall, and the results are shown in the graph of figure 4. The curve follows the same general trend as do those for the other materials, and it can be seen that the difference between the ratio for θ = 0° and θ = 180° is quite significant and of the order of 13 %.

A closer examination of the curves in figures 3 and 4 suggests that the angle θ at which the emission from the wall under investigation is equivalent to that from the graphite wall increases with decrease in atomic number of the wall. The next experiments were intended to examine this point more closely.

(c) *Relation between the angle θ for "equivalent emissions" and atomic number of wall material*

In the experiments, comparative measurements were made similar to those of (b), but they were extended to wall materials covering a wider range of atomic numbers, and only that portion of the curve was investigated which indicates
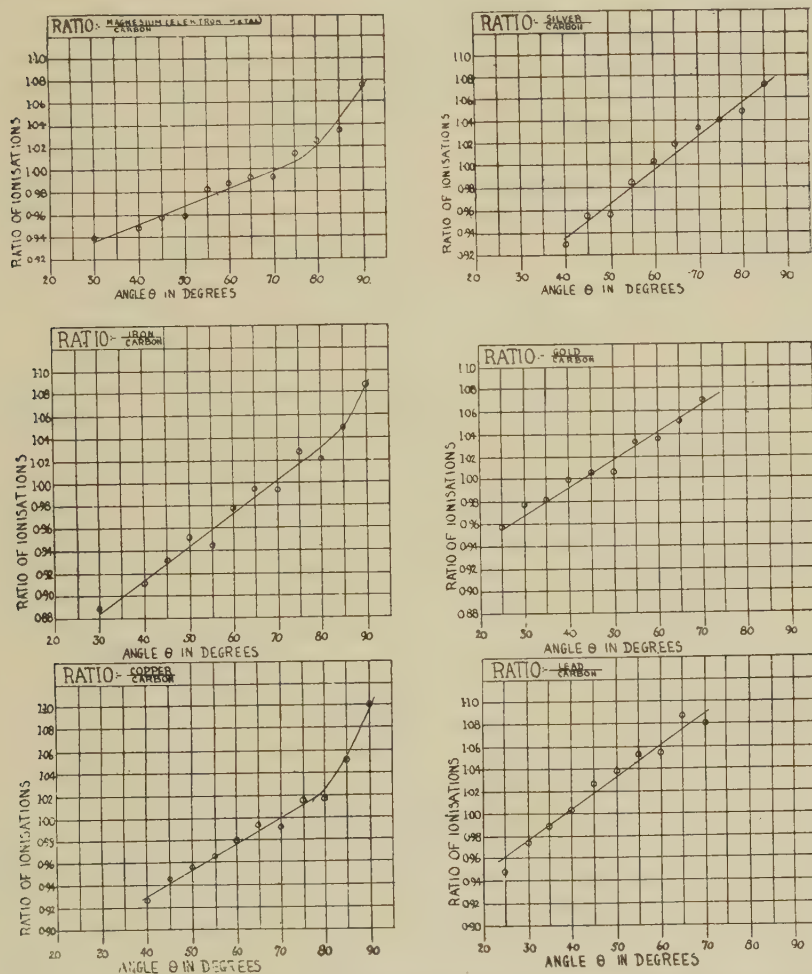
Figure 5.   Relations between θ and the relative electronic emissions for various materials in the region of equivalent emission.

that the emission from the wall material is equivalent to that from the graphite wall.   In order to fix the curves more definitely than in the previous experiments, readings were made with smaller angular spacings between them.   The results thus obtained are summarized in the graphs of figure 5, each graph showing the same relation as was expressed in figures 3 and 4 for the particular wall material

indicated.* Table 2 shows the values of θ for equivalent emissions collected together from these curves. The variation of the angle for equivalent emission with atomic number of the emitter is shown in figure 6.
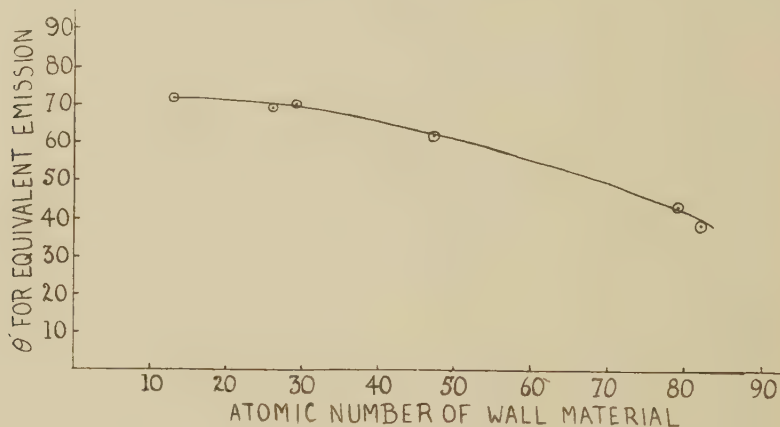

Figure 6. Relation between atomic number of material and the angle θ for emission equivalent to graphite.

Table 2. The angles θ for " equivalent electronic emissions " from various materials

Wall material W	Atomic number Z	θ for emission equivalent to graphite (degrees)
Elektron metal	13	71·5
Iron	26	69
Copper	29	70
Silver	47	62
Gold	79	43·5
Lead	82	38

It would appear that the angle for equivalent emission does definitely decrease as the atomic number of the emitter increases.

§4. DISCUSSION

The significance of the results described above can be appreciated in a general way by making reference to a formula deduced by Mayneord (1930), who showed that when a beam of radiation of short wave-length falls on a plane sheet of material of thickness r, equal to the maximum range of the secondary electrons generated in the sheet, then the secondary electronic emission W is given by

$$W = (\tau + \sigma_a)I_0{}^{\frac{2}{3}}r,$$
$$\ldots\ldots(1)$$

* Strictly, small corrections should be made to allow for gamma-ray absorption in the walls, but because they are very indefinite such corrections have not been attempted. Also, the angle θ is strictly the mean of a small range of angles.

where I_0 is the intensity of the incident radiation, τ the photo-electric absorption coefficient and σ_a is the true absorption coefficient associated with scattering.

To a first approximation r is inversely proportional to the density ρ of the material, so that W is proportional to $(\tau/\rho + \sigma_a/\rho)$. But if ${}_e\tau$ and ${}_e\sigma_a$ are the respective photo-electric and scatter absorption co-efficients per electron, then

$$\frac{\tau}{\rho} = {}_e\tau \cdot \frac{NZ}{A} \quad \text{and} \quad \frac{\sigma_a}{\rho} = {}_e\sigma_a \cdot \frac{NZ}{A},$$

where Z is the atomic number, A is the atomic weight, and N is Avogadro's number.

Thus we may write

$$W \propto ({}_e\tau + {}_e\sigma_a) \cdot \frac{Z}{A}. \qquad \ldots\ldots(2)$$

But when the emission from one side of the sheet only is being considered, it would seem that equation (2) should be modified to

$$W \propto (f_1\,{}_e\tau + f_2\,{}_e\sigma_a) \cdot \frac{Z}{A}, \qquad \ldots\ldots(3)$$

where f_1 and f_2 are the fractions of the total photo-electric and recoil emissions which are emitted in the particular direction with which we are concerned. X-ray evidence (Compton and Allison, 1935) suggests that the fraction f_1 for emergence emission is practically the same as for incidence emission, especially as we are concerned with very short wave-lengths, and the thickness of material will give rise to diffusion of the electrons in the material. Thus, since the sheets are relatively thin, the fraction f_1 for both emergence and incidence emission will be approximately one-half. The fraction f_2 is related to the known " Compton " scattering laws for gamma radiation, so that its value in the case of the incidence emission (backward recoil electrons) will only be a small percentage of the value for emergence emission (forward recoil electrons). Equation (3) then serves to explain the relations of emergence and incidence emissions with atomic number. With increase in atomic number, the increase in ${}_e\tau$ will increase the factor $(f_1\,{}_e\tau + f_2\,{}_e\sigma_a)$, while the factor Z/A decreases. In the case of emergence emission, the total increase in the first factor is smaller for the lower atomic numbers than the decrease in the second factor, so that a net decrease results in a movement towards a minimum, beyond which the effective increase in the first factor is greater than the decrease in the second factor, due mainly to a more rapid increase of ${}_e\tau$ with atomic number. For the incidence emission, however, $f_2\,{}_e\sigma_a$ is much smaller than in the other case, so that the effective increase in $(f_1\,{}_e\tau + f_2\,{}_e\sigma_a)$ is continuously greater than the decrease in Z/A; thus a continuous increase in emission takes place. If a harder gamma-ray beam had been used, the effect of the variation in ${}_e\tau$ would be even smaller, and a more pronounced minimum would occur in the emergence emission. This was found by Stahel (1932) when he increased the filtration of his radium source. If the radiation is of x-ray wave-length, the changes in ${}_e\tau$ are large enough to outweigh the effect of the decrease in Z/A, so that a continuous increase in emission takes place with atomic number.

Similarly, in a general manner, equation (3) affords an explanation of the " equivalent emission " results. We find that at some angle θ, the emission from a graphite (carbon) wall is equivalent to that from a wall with atomic number Z, i.e.,

$$W_{\text{carbon}} = W_Z \text{ at the angle } \theta.$$

Then $W_{\text{carbon}} = f_2 \, {}_e\sigma_a \cdot \dfrac{Z_{\text{carbon}}}{A_{\text{carbon}}}$, since ${}_e\tau$ for carbon is negligible and f_2 is the requisite fraction for the angle θ.

$W_Z = (f_1 \, {}_e\tau + f_2 \, {}_e\sigma_a) \dfrac{Z}{A}$, where f_1 is the fraction of ${}_e\tau$ that is emitted at the angle θ. Thus

$$f_2 \, {}_e\sigma_a \cdot \frac{Z_{\text{carbon}}}{A_{\text{carbon}}} = (f_1 \, {}_e\tau + f_2 \, {}_e\sigma_a) \cdot \frac{Z}{A},$$

whence

$$f_1 \, {}_e\tau \cdot \frac{Z}{A} = f_2 \, {}_e\sigma_a \left(\frac{Z_{\text{carbon}}}{A_{\text{carbon}}} - \frac{Z}{A} \right), \qquad \ldots\ldots(4)$$

i.e. at this angle the photo-electric emission from the wall of atomic number Z just balances the decrease in recoil emission due to the decrease in Z/A (which

SOFT TISSUE   BONE   SOFT TISSUE

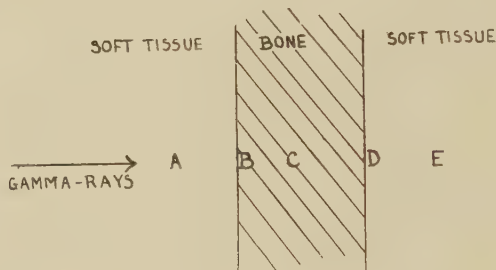GAMMA-RAYS $\longrightarrow$ A   B C   D   E

Figure 7.

corresponds to a decrease in the number of scattering electrons per unit mass). Any more detailed investigation of the results can hardly be attempted, in view of the fact that the radiation used does not constitute a parallel beam, and the size of wall that was used permits the entry to the chamber of electrons at angles other than those specifically considered. In addition, for the larger values of θ, additional absorption in the wall materials will occur, and it is hardly possible to allow for this satisfactorily.

Finally, some of the results described afford some information concerning the probable magnitudes of the relative energy absorption per röntgen of gamma radiation at the boundaries between soft tissues and bone. Thus, consider the case indicated in figure 7, which represents a beam of gamma radiation passing through from soft tissue to bone and out again into soft tissue. Any point that may be considered must strictly be surrounded by equilibrium thickness of material. At point B on the boundary of tissue and bone, where the total emission received may be considered as emergence emission from tissue and incidence

emission from bone, the energy absorbed might be up to 5 % greater than at the points A and E situated wholly within tissue. At D, however, where the emergence emission is from bone and the incidence emission from tissue, the energy absorption per röntgen might be as little as 93 % of that in tissue alone. At a point C situated wholly within bone, the energy absorption per röntgen will be some 5 to 6 % greater than that in tissue.*

§5. ACKNOWLEDGEMENTS

Note added 24 *June* 1941

The author takes the opportunity of acknowledging a suggestion by the referee that on account of the fact that the measurements of emission are the sum of emissions from the wall material and the rest of the chamber, differences instead of ratios might have been preferable as a record of the results. Such a procedure would appear to be more definite, but the absolute values of the differences depend on the radiation intensity at the chamber, that is, upon the distance between the radium source and the chamber. Since it was extremely difficult to standardize this distance exactly, it was not attempted. If the results are corrected to correspond to one initial set of conditions so that differences can be used, the slight ambiguities present in the ratios still exist, and, in effect, the differences would state the excess or deficiency of emission compared with that for the initial conditions. This is little different from the ratios.

In any case, most interest centres around the case where the ratios are nearly unity, so that it appears that the use of ratios is as good as that of differences.

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* It is taken that tissue and graphite are approximately equivalent in their interaction with gamma radiation, while the energy absorption at C, wholly within bone, is based upon the observation that bone and elektron metal behave in much the same way as one another.

REVIEWS OF BOOKS

Introduction to Electricity and Optics, by N. H. FRANK. Pp. xii + 398. (London: McGraw-Hill Publishing Co., Ltd., 1940.) Price 24s. 6d.

This is a textbook written primarily for students of an American Institute of Technology after attaining a certain standard in their course in physics or engineering. Allowing for the differences in the courses of instruction in the two countries, the scope and standard of the work may be described by saying that it is a textbook suitable for degree students of physics and that it is especially to be recommended for honours students in this subject. The work is quantitative in character, the chief aim being to state the laws of the electromagnetic theory accurately and to carry out the deductions from them by methods which are useful in the next stage of the study.

The choice of subjects treated in the book, including a final chapter on *Heat Radiation*, is influenced by the author's wish to expound the unification introduced by means of Maxwell's equations. This exposition is carried out with clarity and without difficulty. The work is easy to read, and one may deduce from the form and logic of its presentation that the author enjoys teaching the subject. A particular feature is the treatment of magnetic problems by means of currents instead of by magnetic poles. Thus magnetic induction is defined by means of the force exerted on a current element, and this procedure is no more troublesome than that previously adopted, and leads to a clearer understanding of the electromagnetic theory. This method of instruction appears to be gaining ground in America and is one which might with advantage be more widely adopted in this country.

The author makes use of certain terms which are not very widely known to describe electrostatic and electromagnetic units. Thus the electrostatic unit of charge is described as the " stat coulomb " and the unit of intensity as the " statvolt per cm.", while the electromagnetic unit of current is called the " abampere." It is recorded that Boltzmann once replied to a criticism of literary style with the retort that style was a matter for the tailor and hairdresser. No such authority has arisen in defence of scientific terms which are an offence to the eye or to the ear, and we may hope that they will become extinct by neglect. They seem almost to mar this excellent book with its eloquence of exposition.

After dealing in the first part of the work with the systematic development of the fundamental laws, the author treats the electric and magnetic properties of matter on the basis of the electron theory in the second part. He has included a useful chapter on Geometrical Optics with short notes on aberration which are quite adequate at this stage of instruction. The chapters on Physical Optics, although brief, are very clear and will be found helpful by the student.
H. T. F.

Physics of the Air, by W. J. HUMPHREYS. (Third Edition.) Pp. xiv + 676. (London: McGraw-Hill Publishing Co., Ltd., 1941.) Price 42s.

Although its title might suggest that this book is yet another textbook of meteorology, actually it differs from them in being addressed primarily to the physicist. Thus instrumental details, important only to the observer, are passed by ; weather forecasting is not touched upon ; the descriptions of different types of cloud are deferred until well on in the book, long after the first references to several of them.

What it *does* contain is a physical treatment, so far as theory is available, of all the various phenomena associated with the air. The physics is sometimes apparently weak, but usually this is a result of imperfect power of expression, and the weaknesses can usually be removed by translating the passage into more familiar physical terms.

The book is divided into five parts, of which the first deals mainly with the temperature, pressure and velocity of the air. The sketch of the state of affairs actually observed is very clear, and (perhaps even more important) it provides the physicist with a source from which he can take data. To those who are not specialists, neither the media of publication nor the power of critical selection are available without some such book as this. This first part deals with the whole question of atmospheric circulation, from the large-scale trade winds to local winds in valleys. It also contains a chapter on evaporation and condensation and one on fogs and clouds. Its last two, on thunderstorms and lightning, form a bridge between Part 1 and Part 2, which is headed *Atmospheric Electricity*. This part seems to need more revision than it has yet received, and in particular the treatment of penetrating radiation is more appropriate to the outlook of 1914 than of 1941.

Parts 3 and 4 summarize respectively our knowledge of meteorological acoustics and atmospheric optics, whilst Part 5, on *Factors of Climatic Control*, is a most interesting account of the various theories which have been put forward to account for ice ages. The author favours a theory which attributes a great part of the changes in climate to the variation of dust (and hence of absorption) in the atmosphere.

There are a few misprints and errors : thus, on p. 98, reference is made to a table which the reviewer has failed to locate. On p. 420, $\dfrac{1 \cdot 40 - 0 \cdot 1e}{P}$ should be $1 \cdot 40 - \dfrac{0 \cdot 1e}{P}$, a slip which might mislead the unwary. But these are minor points. As a whole, the book can be recommended in the double capacity of a readable account and a book of reference.

<div align="right">J. H. A.</div>

Proceedings of the American Philosophical Society, Philadelphia, U.S.A., Vol. 84, No. 2, pp. 125–361. Commemoration of the life and work of Alexander Dallas Bache and Symposium on Geomagnetism, Feb. 14–15, 1941. Price $1.50

Alexander D. Bache, 1806–1867, born in Philadelphia, a great-grandson of Benjamin Franklin, in 1843 became the second head of the United States Coast Survey, after having been Professor of Natural Philosophy and Chemistry at the University of Pennsylvania. In 1836 he had been elected President of Girard College, an educational institution for orphans founded by the will (1833) of a wealthy French-American citizen ; the College was not opened till 1847, but Bache paid a visit to Europe (1836-8) to study educational systems, and his distinguished ancestry gave him the entry to scientific circles in Britain and on the continent. In those days, a century ago, under the influence of Humboldt, Gauss, Weber, Airy and Sabine a great revival of interest in the earth's magnetism was in progress : the Göttingen Magnetic Union was formed, and magnetic observatories were instituted at Göttingen, Greenwich, in the British Colonies, and many other places. Bache became deeply interested in these efforts, and on his return set up a magnetic observatory at Philadelphia, which was continued for several years ; he discussed the results with zeal and ability in a number of memoirs. Later, as Superintendent of the U.S. Coast Survey, he began the scientific development

of magnetic survey work in America. His magnetic researches, and his services in connection with many important American societies and institutions, were commemorated early this year at Philadelphia at a two-day meeting of the American Philosophical Society ; the proceedings included several commemoration addresses, and a geomagnetic symposium at which papers were read by Gish, Heck, McNish, McComb, Johnston, Fleming, Gartlein, Berkner, Hallborg and Heyl.   S. C.

The Physics of Blown Sand and Desert Dunes, by R. A. BAGNOLD.   Pp. xx + 265
    (London: Methuen and Co., Ltd., 1941.)   Price 24s.

Since Wilhelm Schmidt, in 1925, applied diffusion formulae to natural phenomena as diverse as the transport of silt by rivers and the distribution of pollen in the atmosphere, a whole literature has appeared on investigations into natural processes which may be described in terms of an *Austausch* or exchange coefficient.

Surprisingly, the author of this book dismisses diffusion in a short section, as he holds that the mechanism of blown sand is rather by saltation or bouncing over the ground than by turbulent diffusion.   While it is true that sand falls freely at a much higher speed in air than in water, one would have thought that the considerable quantity of the smaller grains held in suspension by the wind would play a greater part in desert morphology than the conclusions of this work indicate.

Lt.-Col. Bagnold has had unique opportunities for studying the forms and movements of sands in the North African deserts.   To experimental physicists who hold that no useful work can be done away from the equipment of a modern laboratory, it will come as a surprise to see how well the phenomena of Nature's huge open-air laboratory can be scaled down to the experiments in a small indoor wind-tunnel and how the author can strip a very complex problem of its unessential features down to its fundamentals.   The book is in the nature of an interim report ; much remains to be done and some fascinating extensions of the study are suggested, particularly in the final chapter, which is no more than a foretaste of work on " singing sands ", interrupted by the outbreak of war.   (Incidentally, why are Eigg and North Wales always cited in this connection, as though they were unique in the British Isles ? The reviewer has found whistling sand *somewhere* on every dry sandy beach that he has examined in England, from Berwick to Grange).   E. G. R.

Principles and Practice of Chromatography, by L. ZECHMEISTER and L. CHOLNOKY ;
    translated by A. L. BACHARACH and F. A. ROBINSON, with a Foreword by
    Prof. I. M. HEILBRON.   Pp. 362.   (London: Chapman and Hall, Ltd.)
    Price 25s.

In 1906 Tswett carried out a simple and interesting experiment.   He extracted some green leaves with light petroleum and poured the extract through a vertical column of powdered calcium carbonate.   He found that after the passage of the liquid there remained a yellow ring in the upper part of the column.   Below this ring were two green zones and, farther down, three other yellow bands.   Thus the science of chromatography was born.

This volume presents an excellent account of the varied applications of the method. It is clear that the organic chemist interested in the fields of the natural pigments, vitamins or hormones is provided with an invaluable tool.   To those who are interested in the physics and physical chemistry of adsorption, a whole host of new and interesting

problems awaiting solution are presented. Whilst the phenomena of ionic adsorption and ionic exchange adsorption are comparatively well known, we are still very much in the dark as to the quantitative evaluation of the dispersive forces or Van der Waals fields exerted by complex organic molecules. It is these forces that are largely operative in chromatic analysis. The exact evaluation of the adsorption potential of, for instance, a benzene ring by examining the partitions of a homologous series of organic compounds, whilst simple in principle, is not so easy in practice, as problems of molecular configurations immediately intrude.

To those interested in the problems of dyeing the book will be of interest and value. Even in the case of wool dyeing the simple concept of salt formation is not sufficient to account either for the fastness or amount of dye taken up ; the dispersive forces play a large part in the process. This volume provides us with methods by which these can be explored.

<div align="right">E. K. R.</div>

The Scientific Journal of the Royal College of Science. Vol. XI. Pp. vi + 94. (London: Royal College of Science, 1941.) Paper, 4s.; cloth, 5s. 6d.

This journal records the activities of the Imperial College Chemical Society and the R.C.S. Mathematical and Physical Society. Students who have the opportunity to attend lectures of the type reported here, gain something difficult to define, which cannot be provided by the more formal lectures of a college course. Others can, as a substitute, read the lectures as now printed, and they would be well advised to do so.

The lectures range over a variety of topics (it is interesting to note that the four chemical lectures are on physical subjects—crystallization, polarimetry, thermal diffusion and adsorption), and are remarkable for the modernity of subject and treatment. An article on separation of isotopes has 20 references, of which 12 are to papers published in 1940. Chromatographic analysis, the subject of another lecture, is so new that many physicists will not know the name ; the first English book on the method, which is the separation of substances by making use of differential adsorption, was only published this year.

The volume, though thinner than in pre-war days, is well produced and does credit to all concerned with its preparation and publication.

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ERRATUM

This volume, p. 250 (paper by WILSON and LIPSON), table 4, seventh column, fifth and sixth entries : *for* 72·803 *read* 73·803 and *for* 72·092 *read* 75·092.

RECENT REPORTS AND CATALOGUES

Dielectric Properties of Experimental Resin-Paper Boards, by L. HARTSHORN and E. RUSHTON with N. J. L. MEGSON. (Technical Report L/T100, 1941.) THE BRITISH ELECTRICAL AND ALLIED INDUSTRIES RESEARCH ASSOCIATION, 15 Savoy Street, London, W.C. 2. 2s. 10d. inclusive of postage.

Dielectric Loss in Dipolar Solids. I—Solutions of Dipolar Molecules in Solid Paraffins, by H. FRÖHLICH. (Technical Report L/T121, 1941.) Pp. 12. THE BRITISH ELECTRICAL AND ALLIED INDUSTRIES RESEARCH ASSOCIATION, 15 Savoy Street, London, W.C. 2. 11s. 9d. inclusive of postage.

War Emergency British Standard Specification for Identity Photographs. (No. 967, June 1941.) Pp. 6. BRITISH STANDARDS INSTITUTION, 28 Victoria Street, London, S.W. 1. 2s. 3d. inclusive of postage.

A Short Catalogue of Mathematical and Physical Books. (No. 212.) Pp. 14. GALLOWAY AND PORTER, LTD., Cambridge.

Consultant Facilities. Pp. 8. (Reprinted from *The Industrial Chemist*.) MURRAY, BULL AND SPENCER, LTD., 20 Kinnerton Street, Wilton Place, Knightsbridge, London, S.W. 1.

Rubber and its Engineering Uses, by (the late) B. D. PORRITT. Pp. 16. (May 1941.) THE BRITISH RUBBER PUBLICITY ASSOCIATION, 19 Fenchurch Street, London, E.C. 3.

Annotated Catalogue of Works on Exact and Applied Science. (No. 868, 1941.) Pp. 120. HENRY SOTHERAN, LTD., 2–5 Sackville Street, London, W. 1.

The Wild-Barfield Heat-Treatment Journal (Economy Issue), vol. IV, no. 29, pp. 47–54, June 1941. WILD-BARFIELD ELECTRIC FURNACES, LTD., Watford, Herts.

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REPORT ON BAND SPECTRA OF DIATOMIC MOLECULES. By W. JEVONS, D.SC., Ph.D. (1932). Price: bound in cloth, 21s.; in paper covers, 18s.

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